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May 20, 1998

ONR Code 335
Dr. Eric Eisenstadt
Office of Naval Research
800 North Quincy Street
Arlington VA 22217-5660

Dear Dr. Eisenstadt:

ONR Grant: N00014-97-1-0498

Enclosed is the Final Technical Report for Symposium V,
"Interfacial Effects and Organization of Inorganic-Organic
Composite Solids," held at the 1997 MRS Spring Meeting and
supported by ONR Grant N00014-97-1-0498.

If you have any questions or require additional information,
please contact me.

Sincerely,

Donna J. Gillespie
Donna J. Gillespie
Symposium Funding Administrator
gillespie@mrs.org

Enclosure

cc: Defense Technical Information Center (w/enclosure)
Grant Administrator, Chicago Office (wo/enclosure)

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Part I - Summary of Completed Project

Symposium V, "Interfacial Effects and Organization of Inorganic-Organic Composite Solids," focused on recent applications in materials synthesis that use structure-directing agents and self-assembly phenomena to manipulate inorganic-organic interfaces and control the structure of composite materials. Molecular agents and their supramolecular counterparts have become important species for defining the structure and properties of these hybrid materials. Processes such as adsorption, aggregation, and crystallization that rely on the interplay of simple intermolecular forces are key factors in establishing the structure and properties of the resulting materials; biomimetic approaches also apply here. The association properties of these (primarily organic) molecules -- either to each other or to an inorganic phase -- strongly influence the characteristics of the inorganic-organic interface and the properties of the material. Exquisite control over these organic precursors -- in terms of their shape, size, uniformity, function, and chemical attributes -- is based on the ability to manipulate the attributes of molecules and supramolecular assemblies. The ability to define and controllably manipulate the chemical architecture of these structure-directing agents provides opportunities for exploring structure-property relationships at the atomic/molecular level across a broad range of areas. The uniting factor that spans research in these different areas of directed materials synthesis has been the ability to control and manipulate inorganic and mixed inorganic-organic structures by the assembly of well-defined molecular precursors.

The objective of this forum was to explore underlying paradigms of molecular design as they impact structure-directed syntheses of inorganic-organic composite materials. Topics of particular interest include those that relate materials properties to the molecular attributes of the organic structure-directing agents. The organizers sought to bring together investigators from the various communities in order to define common attributes of these strategies and promote their application in new areas of materials science.

Topics of particular interest included:

- Biomaterial materials
- Heterogeneous ceramics and polymers
- Inorganic-surfactant mesophases
- Molecular templating
- Inorganic-organic thin films
- Inorganic-organic multilayer structures and layered materials
- Crystal growth at solid surfaces

Part II - Technical Information

Please see attached Abstracts.



SPRING '97

1997 SPRING MEETING

MARCH 31- APRIL 4, 1997
SAN FRANCISCO, CALIFORNIA

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ABSTRACTS

MRS meeting information is available on the MRS Website:
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SYMPOSIUM V

Interfacial Effects and Organization of Inorganic-Organic Composite Solids

March 31 - April 2, 1997

Chairs

Brad Chmelka
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Symposium Support
Army Research Office

• Invited paper

SESSION V1: ORDERED MICRO- AND
MESOPOROUS INORGANIC OXIDES

Chair: Brad D. Chmelka
Monday Morning, March 31, 1997
Nob Hill C

8:30 AM *V1.1

TAILORING THE PORE SIZE OF MOLECULAR SIEVES BY
SYNTHESIS AND MODIFICATION TECHNIQUES, J. C. Vartuli,
C. T. Kresge, W. J. Roth, Mobil Technology Company, Paulsboro, NJ.

Porous inorganic solids have found great utility as catalysts and sorption media because of their large internal surface area. Microporous materials, containing pore diameters of $< 20 \text{ \AA}$, are exemplified by crystalline framework solids such as zeolites. Because of their unique pore systems, these crystalline materials can impart shape selectivity for both the reactants and products when processing relatively low molecular weight hydrocarbon feedstreams. For processing large molecules, mesoporous ($\sim 20 - 500 \text{ \AA}$ pore diameters) amorphous solids, such as silica or alumina, or pillared layered materials have been the available materials. However, molecular size exclusion or shape selective processing is not as readily obtained on amorphous solids because they usually have a broad distribution of pore sizes. Recently Mobil has announced the discovery of two new classes of materials, having tunable pore systems in the mesopore range, that offer the potential shape selective processing of larger molecules. These are the M41S family of mesoporous molecular sieves and MCM-36, a pillared molecular sieve with zeolitic properties. The tunable pore system of these new materials allows for the construction of specific pore size and molecular sieve structure that has not been achieved in microporous systems and offers the ability to tailor make materials for specific processing needs. The synthesis and characteristics of these novel materials will be discussed in the perspective of classical porous materials.

9:00 AM *V1.2

ORDERED MESOPOROUS SILICAS AND ZIRCONIAS: CONTROL
ON LENGTH SCALES BETWEEN NANOMETER AND
MILLIMETER, Ferdi Schuth, Ulrike Ciesla, Stefan Schacht, Meike Thieme, Johann Wolfgang Goethe-Univ Frankfurt, Inst für Anorganische Chemie, Frankfurt, GERMANY; Galen D. Stucky, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA.

Ordered mesoporous solids, the most well known example being the MCM-41, can now be prepared with a variety of inorganic frameworks and various different types of surfactants. The highest quality materials with respect to thermal stability and perfection of the structure seem to be the silicas and the zirconias. Materials properties can vary substantially, depending on the mode of preparation. For instance, silica samples synthesized from acidic media have a conventional pathway under alkaline conditions. The stability and pore sizes of zirconias depend strongly on the amount of sulfate present in the synthesis mixture, which controls the degree of condensation of the structure. For both systems, the synthesis starting with the alkoxides provides morphological control on the micron to millimeter length scale if an auxiliary hydrophobic organic solvent is used. Due to the better solubility of the alkoxides in the organic phase, an emulsion forms, with the surfactant molecules concentrated in the interface. Hydrolysis of the alkoxides then takes place at the interface, where the mesostructure forms. The presence of the interface then controls the morphology of the resulting mesostructured oxide particles. Following such pathways, spherical particles of mesostructured silicas and zirconias can be prepared, either as hollow or as solid spheres. For the silica, also flat sheets can be formed at a static interface.

9:30 AM V1.3

ENERGETICS OF MICROPOROUS TEMPLATE-MEDIATED
OXYFLUORINATED MATERIALS, Corine M. Gerardin, Alexandra Navrotsky, Princeton Univ, Dept of Geosciences, Princeton, NJ; Thierry Loiseau, Inst Lavoisier, Versailles, FRANCE; Gerard Ferey, Univ de Versailles, Versailles, FRANCE.

To increase our understanding of how organic molecules act as structure directing agents in the formation of microporous materials, we launched an investigation of the energetics of a series of oxyfluorinated microporous compounds using high temperature solution calorimetry with lead borate solvent at 979K. Microporous ULM-n phases form in the systems M_2O_3 ($M = \text{Al, Ga}$)/ P_2O_5 /AF ($A = H^+, NH_4^+$)/amine/ H_2O under hydrothermal conditions. Various three dimensional crystalline phases were synthesized depending on the nature of the amine and the pH of the starting mixture. To examine the relative stability of these compounds, a thermochemical study was undertaken on different structures where the templates are amines of different pKa, lengths and shapes. The goals are to determine the stability of the inorganic frameworks and also the stabilization energy arising from the

interaction between the templates and the framework. The first results were obtained on the ULM-3 microporous compound $(GaPO_4)_3F(OH) \cdot 1DAP \cdot 1H_2O$ where the template was the hydrated form of diaminopropane (DAP). Transposed temperature drop calorimetry experiments were run first at 979K and yield a decomposed product with a collapsed structure. This decomposed product was characterized further and then studied by drop solution calorimetry: it is only 14 kJ/mol $GaPO_4$ less stable than cristobalite $GaPO_4$. The enthalpy of formation at 298K of the templated microporous compound relative to cristobalite, amine and water in the liquid state is about -200 kJ/mol $GaPO_4$. This large exothermic enthalpy of formation may come from the interaction between diaminopropane and water and/or from the interaction between the template and the framework. A combination of high temperature calorimetric experiments and the investigation of different ULM-n compounds templated with amines, hydrated or not, and of different lengths, will lead to a better understanding of the stability of these microporous structures and a better knowledge of the interaction energies between the different parts of these organized organic-inorganic materials.

10:15 AM *V1.4

UTILIZING CLUSTERS IN THE FORMATION OF MESOPOROUS
MATERIALS, Brian T. Holland, Andreas Stein, Univ of Minnesota,
Dept of Chemistry, Minneapolis, MN.

Mesoporous materials have been prepared by utilizing clusters of the $AlO_4A_{12}(OH)_{24}(H_2O)_{12}^{7+}$ Keggin-like ion. The clusters are ordered by the addition of surfactants such as sodium dodecyl sulfate (SDS) and dodecyl benzene sulfonic acid (DBSA). Once ordered, the clusters can be linked through condensation reactions or through an added component, i.e., tetraethyl orthosilicate (TEOS) and phosphate linkages. Removal of the surfactant leads to an open pore system. In the final material, the clusters are either broken down into low-molecular-weight aluminum species or remain intact, each of which offers unique characteristics. The ordered nanocomposite materials are either two- or three dimensional network materials that are distinguished by clusters that form an integral part of the network. Materials such as these have the advantage of high surface area and increased porosity, along with high charge density regions in TEOS-treated samples. These clusters are used as model compounds to design cluster materials based on V, Mo, and W polyoxometallates, with potential applications as redox catalysts and substrates for biochemical separations along with applications in electrochromic or solid-electrolyte devices.

10:45 AM V1.5

SYNTHESIS OF SELF-ASSEMBLED FUNCTIONAL MOLECULES
IN MESOPOROUS MATERIALS (II); CONDUCTIVE MESOPHASE
BY SELF-ORGANIZED CERAMIC/POLYMER COMPOSITES,
Itaru Honma, Electrotechnical Laboratory, Energy Div, Ibaraki,
JAPAN; Hao-shen Zhou, RIKEN, Saitama, JAPAN.

The functional opto-electric materials with molecular-to-nano size structure has attracted much attention for devices with excellent properties. We present, in this paper, a new synthetic route of self organization process to produce self-assembled molecules doped in mesoporous materials. The synthesis was examined in two ways. The first one is by using dye-bound surfactant; Ferrocenyl TMA as well as diacetylene incorporated surfactant was used as a co-assembly surfactant to silicate framework in spite of C16TMA for silicate MCM. The product was assigned new class of MCM, which is colored as prepared and has optical absorption band in a visible light region because of that the self assembled surfactant itself has photo-absorbing dye either in the middle or at the tail of the lipid molecule. Transmission electron micrograph (TEM) shows clear hexagonal array of the MCM channel and low angle XRD analysis showed hexagonal phase with d-spacing of 37 Å. The powder was yellow as synthesized with an optical absorption band centered at around 480 nm and it shifts to 630 nm by oxidation of ferrocenyl-ligand dye. The second one is that the dye-molecule such as Porphyrin was doped in silicate MCM or other metal oxides framework. The hydrophobic Porphyrin molecules were dissolved in C16TMA/ H_2O solution and hydrolyzed with a silicate precursor or other metal oxides precursor. The colored product shows a clear hexagonal phase by XRD analysis and d-spacing of the product was slightly shortened from that of pure silicon MCM. Only hydrophobic molecules were doped within C16TMA micelles and self assembled in the channels. The class of transition metal oxides were used as a MCM framework to have carrier conductivities for the self-organized ceramic/polymer composites. Optical and electrical properties of these products were examined in relation with a mesostructure of the materials.

11:00 AM V1.6

FORMATION OF A SILICATE SPONGE PHASE,
Kathryn McGrath, Sol M. Gruner, Princeton Univ, Dept of Physics,

Princeton, NJ; Ilhan Aksay, Princeton Univ, Dept of Chemical Engr, Princeton, NJ; Daniel Dabbs, Nan Yao, Princeton Univ, Princeton Materials Inst, Princeton, NJ.

The lyotropic sponge phase, a bicontinuous liquid crystal, has been used to produce monolithic silicates. The silicate which forms during condensation is templated by the presence of the liquid crystal and hence may itself be described as a sponge phase. In contrast to aerogels, the templated silicates are continuous in space dividing two subvolumes. The characteristic length scales of the silicates, controlled by the initial composition of the surfactant solution, have been determined using small angle x-ray scattering as indicated by the presence of a peak in the diffraction pattern as a function of q , which is not seen with DLA aerogels. The pore dimensions vary between 10 and 30 nm, correlating well with the dimensions of the original sponge phase. TEM images show a random bicontinuous pattern as expected and BET measurements indicate surface areas between 30 and 500 m^2/g . The monoliths are transparent and optically isotropic.

11:15 AM V1.7

CHIRALLY-TEMPLATED ZINC PHOSPHATE PHASES.

Tina M. Nenoff, Sandia National Laboratories, Catalysis Chemical Technologies, Albuquerque, NM; Steven G. Thoma, Paula P. Newcomer, Sandia National Laboratories, Albuquerque, NM.

Our attempts are to grow crystalline-walled inorganic materials, whose inherited chirality could be applied to separations and catalytic processes. It is the association of the template molecules to each other and to the inorganic phase that directs the transfer of chirality. We present the results of templated Zinc Phosphate crystalline phases, and focus on one new phase with periodic mesoporous characteristics. Characterisation techniques applied to these phases include powder X-ray diffraction, TEM, DCP and BET.

Templates used are primarily amino acids. The crystallization conditions are mild but extremely time, pH and temperature dependent. The crystallization is template dependent also; organic molecules similar in shape and composition will result in porous, layered or condensed crystalline phases.

A periodic mesoporous phase is templated by a chiral molecule approximately 10 in size and its resultant supermolecular assembly contains periodic mesopores on the order of 35, indicating a possible space filling arrangement for the organic molecules.

11:30 AM V1.8

COMPETITION BETWEEN KINETIC AND THERMODYNAMIC CONTROL OF PHASE TRANSITIONS IN SILICA/SURFACTANT MESOPHASE COMPOSITES, Sarah H. Tolbert, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA; Poul Norby, Jon C. Hanson, Brookhaven National Laboratory, National Synchrotron Light Source, Upton, NY; Galen D. Stucky, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA.

Ordered inorganic/surfactant mesophase composites represent a major advance in the synthesis of materials with nanoscale periodicity. The materials are formed by the self assembly of combined inorganic/organic species and represent a unique non-equilibrium solid phase. In an effort to understand the kinetics and thermodynamics that control structure in these materials, we have followed phase transformations in these composites under hydrothermal conditions using real time X-ray diffraction. Transformations in polymerised silica/surfactant composites between hexagonal (P6m), lamellar, and micellar hexagonal (P63/mmc) phases were observed. In all cases, the structural transformations appeared to be driven by packing constraints of the organic component of the composite, suggesting that this organic phase packing plays a dominant role in determining the observed structures of these materials. Similar packing constraints have been used to understand equilibrium structural changes in pure surfactant/water systems. In this case, however, all transformations are intrinsically non-equilibrium, exemplified by the observation that the transitions are not reversible. Thus, while organic packing may control the observed structures of these materials, the cross-linked inorganic component plays a large role in determining transformation energetics. Because of the detailed chemical control available during the synthesis of these materials, it is possible to observe both hexagonal (P6m) to lamellar and lamellar to hexagonal transitions under similar conditions. This offers a unique opportunity to follow both forward and reverse reactions of a transformation that occurs far from equilibrium. Hexagonal to lamellar transformation are discontinuous (1st order) and proceed through a modulated lamellar phase. Lamellar to hexagonal transitions also proceed through a modulated lamellar phase, but in this case the reaction appears to be continuous (likely 2nd order). Implications of this result on the structural stability of these materials as well as a more detailed kinetic analysis of the transformations will be discussed.

SESSION V2: INORGANIC-SURFACTANT MATERIALS

Chair: Ferdi Schuth

Monday Afternoon, March 31, 1997

Nob Hill C

1:30 PM *V2.1

HIERARCHICALLY STRUCTURED ORGANIC/INORGANIC COMPOSITES, Ilhan Aksay, Princeton Univ, Dept of Chemical Engr, Princeton, NJ.

Hierarchically structured organic/inorganic materials with deliberately designed nano- and micro- and centimeter scale features can be fabricated by a combination of patterning methods. At the nanometer scale, patterning of organic/inorganic composites by selfassembly will be illustrated with two examples: First, epitaxial coordination of silica/surfactant tubules on crystalline substrates will be contrasted with a random arrangement observed on amorphous silica. Secondly, a triblock copolymer of polystyrene-polybutadiene-polystyrene will be used to illustrate patterning inorganics with nanoscale modulations. In both cases, the organic self assemblies to form cylindrical nanodomains which are then used to pattern an inorganic phase with nanoscale modulations. The ability to pattern these composites further at micrometer scale by micromolding and at millimeter to centimeter scale by laser lithography provides new technological opportunities. Supported by the Army Research Office and the National Science Foundation.

2:00 PM *V2.2

NANOSTRUCTURING AND PATTERNING OF SEMICONDUCTORS WITH LIQUID CRYSTALS, Samuel I. Stupp, Univ of Illinois-Urbana, Dept of MS&E, Urbana, IL; Paul V. Braun, Paul Osenar, Univ of Illinois-Urbana, Dept of MS & E, Urbana, IL; Valeria Tohver, Univ of Illinois-Urbana, DMS&E, Urbana, IL.

We reported recently direct templating of nanoscale features in cadmium sulfide by precipitation of this semiconductor in an ion-doped lyotropic liquid crystal (Nature, **380**, 325 (1996)). The precipitation process copies the symmetry and characteristic dimensions of a hexagon surfactant mesophase by avoiding growth of CDs within regularly spaced hydrophobic regions. The final product is a hybrid solid in which a CDs continuum is featured with hexagonally arranged cylindrical pores 23-3 nanometers in diameter lined by surfactant molecules. Interestingly, the symmetry of the template can also be expressed on a larger length scale as evidenced by the observation of hexagonal faceting in particles of the hybrid solid. The nature of cations and counterions does affect the crystallinity of the semiconductor, and also the fidelity of nanostructuring by the mesophase. For example, we have been able to template nanostructured ZnS, CdSe, and other ternary phases, but only non featured solids can be obtained in many other metal sulfides. Very recently we discovered the same liquid crystals can be used to pattern the surfaces of soft substrates with micro-features. This suggests the possibility of developing a selfassemblylithography which generates dual scale features in semiconductors.

2:30 PM V2.3

MAGNETIC-FIELD-INDUCED ORIENTATIONAL ORDERING OF SILICATE-SURFACTANT LIQUID CRYSTALS, Ali Firouzi, Univ of California-S Barbara, Dept of Chemical Engr, Santa Barbara, CA; Sarah H. Tolbert, Galen D. Stucky, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA; Brad D. Chmelka, Univ of California-S Barbara, Dept of Chemical Engr, Santa Barbara, CA.

Recent developments of new classes of mesoporous materials, synthesized using surfactant species as structure-directing agents for inorganic frameworks, have provided new links between organic and inorganic synthesis strategies. Specifically, cooperative interactions among multiply charged silicate anions and cationic surfactant species induce assembly of lamellar, hexagonal, and cubic silicate-surfactant mesophases. The liquid crystalline properties of these materials can be exploited to produce macroscopically aligned samples in high magnetic fields. Comparisons of experimental and simulated 2H NMR spectra of deuterated surfactant species quantify the degree of orientational order achieved. The overall orientation of a mesophase with respect to the applied magnetic field depends upon the diamagnetic susceptibilities of the individual molecular species in the multicomponent mixture. As a result, it is possible to control macroscopic alignment of these liquid crystalline systems by tuning their composition: for example, lamellar or hexagonal domains adopt different orientations, according to the diamagnetic susceptibilities of the species present. The macroscopic ordering of silicate-surfactant mesophases, furthermore, introduces attractive opportunities for obtaining aligned inorganic mesoporous materials. After condensation of the silicate species and subsequent removal of the organic components, macroscopically oriented bulk solids result. Prospects for

producing mesoscopically ordered porous materials with alignment over macroscopic length scales remains a powerful driving force for research and new applications, particularly in the areas of catalysis, separations, and patterned-device development. The macroscopic alignment of the silicate-surfactant mesophases shown in this work is believed to be an important step towards achieving these goals.

3:15 PM V2.4

SYNTHESIS OF LAMELLAR AND DISORDERED HEXAGONAL METAL SULFIDE MESOPHASES, Mark T. Anderson, Barret G. Potter, Sandia National Laboratories, Albuquerque, NM.

Novel templated nonoxide/organic framework structures are of interest because many are optically active and electronically conductive, and they can generally be synthesized under mild conditions. Recently, supramolecular templates, i.e., preformed hexagonal liquid crystalline phases, have been used to synthesize II-IV semiconducting frameworks. A major drawback of this approach is that it requires a large excess of expensive surfactant. Here we report the surfactant templated synthesis of a wide variety of metal sulfide/amphiphile mesophases, including those based on Cd, W, Mo, Sn, and Ga sulfide frameworks. The materials are prepared by combining stoichiometric quantities of surfactant and in-situ generated metal sulfide molecules in aqueous solution. Lamellar and disordered cylindrical phases are obtained depending on reaction time, surfactant concentration, pH, and temperature. The materials exhibit optical properties that depend on the interlayer spacing. We believe these surfactant-templated metal sulfides may have useful optical, electronic, and catalytic applications.

This work was funded by the United States Department of Energy under Contract Number DE-AC04-94AL85000.

3:30 PM V2.5

THE EFFECTS OF MATRIX INTERACTIONS ON THE PROPERTIES OF SOL-GEL MATERIALS DOPED WITH BIOMOLECULES, Bruce Dunn, Univ of California-Los Angeles, Dept of MS&E, Los Angeles, CA; Jeffery Zink, Univ of California-Los Angeles, Dept of Chem & Biochem, Los Angeles, CA; B. C. Dave, Southern Illinois Univ, Dept of Chem & Biochem, Carbondale, IL; Joan S. Valentine, Univ of California-Los Angeles, Dept of Chem & Biochem, Los Angeles, CA.

The use of sol-gel materials as host matrices for biological molecules has been well established. The dopant biomolecules reside in the porous network of these sol-gel composite materials as part of a nanostructured architecture. A diverse range of proteins, enzymes, and other biosystems are functionally active in the sol-gel glass and their characteristic reactions are analogous to those in solution with the exception that now the system involves a porous silicate network. In this paper, different examples are given in which pore-biomolecule interactions are studied. Optical absorption, resonance Raman and impedance spectroscopy methods are used to characterize the nature of the physical and chemical interactions between the pores of the SiO_2 matrix and cytochrome c. The results show that noncovalent interactions between the surface of the protein and the pore walls govern the dynamics of pore formation during gelation. The individual biomolecules act as structural templates to design local pore structure. Once the inorganic cage is formed, biomolecule mobility is restricted. This, however, improves the stability of cytochrome c as chemical and thermal pathways for denaturation are avoided. Enhanced stability is also exhibited with sol-gel glass doped with green plant photosystem II (PS II). The photoactivity and photooxidation of water are used to demonstrate that the PS II particles are stabilized by the encapsulation process. The effects of matrix interactions on the reaction kinetics of enzyme catalysis are reviewed for peroxidase and dehydrogenase systems.

4:00 PM V2.6

ASSEMBLY OF ELECTROACTIVE ORGANIC SPECIES IN LAYERED PHOSPHATES, Renal Backov, Univ de Montpellier II, Lab des Agregats Moleculaires & Materiaux, Montpellier, FRANCE; Robert Fourcade, Univ de Montpellier II, Lab des Agregats Moleculaires & Materiaux Inorganiques, Montpellier, FRANCE; Deborah Jones, Univ de Montpellier II, Lab des Agregats Moleculaires et Matia, Montpellier, FRANCE; Bernard Mula, Jacques Rosiere, Univ de Montpellier II, Lab des Agregats Moleculaires & Materiaux Inorganiques, Montpellier, FRANCE; Jean-Marc Fabre, Univ de Montpellier II, Lab de Chimie Organique Structurale, Montpellier, FRANCE.

Layered metal (IV) hydrogen phosphates (forms alpha and gamma) have been used to assemble and spatially organize partially oxidized tetrathiafulvalene (TTF). Formation of conducting organic-inorganic hybrids of TTF and zirconium phosphate (ZrP) requires the use of specific precursor phases. Oxidative intercalation occurs by reaction of gamma-ZrP exchanged with Cu(II) to varying degrees with neutral TTF to give materials in which the amount of TTF inserted and its

partial oxidation state closely depend on the initial Cu(II) loading. ZrP-TTF phases prepared in this way have partial charges of 0.77-0.98+, a TTF loading of 0.1-1.0 and conductivities in the range 10^{-6} to 10^{-4} Scm^{-1} at 25°C. Any further increase requires the lowest partial charge to be maintained while increasing the TTF uptake. This has been achieved by using as precursors alpha or gamma-ZrP preconditioned with long chain alcohols or surfactants. These increase the hydrophobicity of the interlayer region and define an effective ion exchange capacity. The amount of partially charged TTFs inserted then lies in the range 0.7-1.2 TTF/Zr. Raman spectroscopy shows $\text{TTF}^{0.72+}$ to be the unique species confined in the interlayer region. The conductivity of phases derived from alpha and gamma ZrP differ in their temperature dependence, the latter having metallic behavior around room temperature. Both have conductivities of $3-4 \text{ Scm}^{-1}$ at 25°C, higher than that of any other intercalation compound derived from ZrP and rivaling that of any other intercalation hybrid organic-inorganic system. Furthermore, precipitation of colloidal ZrP in the presence of $\text{TTF}^{0.72+}$ leads to the formation of highly oriented, self-supporting films.

4:15 PM V2.7

COLLOIDAL COPPER NANOPARTICLES PRODUCED BY SUGAR BIOSURFACTANTS, M. Thies, U. Hinze, Henrich H. Paradies, Markische Fachhochschule, Dept of Biotechnology & Physical Chemistry, Iserlohn, GERMANY.

Metal colloids may be prepared in a wide variety of chemical and physical environments. The interactions between the metals, e.g., Cu, and the surrounding molecules, e.g., solvents polar vs. apolar, ligands as chiral vs. racemic, surfactants cationic vs. anionic or nonionic, support, also affect the Cu metal cluster properties, and that of each nucleant. In contrast to known methods of producing nanometal particles, which uses strong reducing reagents, e.g., hydrazine in apolar solvents and in the presence of reverted micelles, we report the successful preparation of Cu nanoclusters in the presence of naturally occurring biosurfactants built from glycolipids A & B in an aqueous environment. This method produces nanoclusters of sizes between 2 and 12 nm with a surface plasmon band at 568 nm. The reduction of the copper salts to colloidal copper in the presence of the glycolipids A and B can be enhanced through addition of less than 10 molecules of didocylidimethylammonium hydroxide per biosurfactant micelle. The addition of the cationic surfactant induced a strong increase in the size and in the yield as observed by TEM and light scattering measurements. Due to the low CMC of the biosurfactants including the very low surface tension which is not significantly affected by the cationic surfactant enables one to produce large quantities of Cu nanoclusters.

4:30 PM V2.8

DESIGN, SYNTHESIS AND PROPERTIES LAMELLAR POLYMER/INORGANIC NANO-COMPOSITES,

Mercoun G. Kanatzidis, Lei L. Wang, Michigan State Univ, Dept of Chemistry, East Lansing, MI; Jon L. Schindler, Carl R. Kannewurf, Northwestern Univ, Dept of E&CE, Evanston, IN; Hui-Lien Tsai, Michigan State Univ, Dept of Chemistry, East Lansing, MI.

Well ordered organic-inorganic multilayer structures are formed with polyethylene-oxide (PEO) and other functional polymers and layers of MoO_3 , MoS_2 , WS_2 , TaS_2 and NbSe_2 . These hybrid materials exhibit combinational properties which are not observed in physical, two-phase mixtures of the individual components. The TaS_2 and NbSe_2 nano-composites with PEO and polyvinylpyrrolidone can exist as large free-standing films which undergo superconducting transitions while possessing plastic like properties. The T_c of PEO- NbSe_2 is at 7.0 K in contrast with the significantly smaller T_c of previously reported molecular or atomic intercalates of NbSe_2 . The nature of the polymer-layer interactions and the factors responsible for the stabilization of these hybrid materials depends on the surface structure of the layers and the electronic properties of the inorganic phase. In some cases these interactions can lead to a complete endotaxial order of the polymer chains. The optical, electrical and magnetic properties of these multilayer structures will be discussed.

4:45 PM V2.9

INFLUENCE OF IMIDIZATION METHOD AND ALKOXIDE COMPOSITION ON THE MORPHOLOGY AND PHYSICAL PROPERTIES OF POLYIMIDE-INORGANIC SYSTEMS,

Patricia R. McDaniel, NASA Langley Research Center, Hampton, VA; Terry L. St. Clair, NASA Langley Research Center, Composites & Polymers Branch, Hampton, VA.

The production of organic-inorganic hybrid materials may take place through several different methods. One of the most popular modes has been through sol-gel processes where the organic and inorganic phases are commingled in solution, then cured. Polyimide-inorganic hybrids are formed in-situ from the hydrolysis of the polyimide acid precursor during imidization, which is accompanied by the polycondensation of

a metal alkoxide. Traditionally, polyimide-inorganic ceramics formed through sol gel routes have involved the formation of transparent or translucent thin films where the small inorganic particles are dispersed in a film. Another widely used method of generating organic-inorganic blended materials is by microencapsulation. This technology is being used extensively in many industries and for a wide variety of materials. As a result of agglomeration, traditional methods of encapsulating metal oxide particles results in a multimolecular/multinuclear core region surrounded by a coating. A method utilizing sol-gel precursors in conjunction with microencapsulation technology has resulted in the formation of a metal oxide as a discrete particle thinly coated with a polymer. The physical characteristics and morphology of the polyimide-inorganic powders have been found to be highly dependent on the chemical composition of the metal alkoxide and the method of imidization employed. Polyimide-silicate, polyimide-titanate and polyimide-zirconates have been produced by four differed imidization methods. Each morphology was examined by SEM; thermal properties determined by Differential Scanning Calorimetry, Thermal Gravimetric Analysis, and Thermal Mechanical Analysis; along with determining bulk mechanical properties.

SESSION V3: INORGANIC-ORGANIC THIN FILMS

Chair: Paul E. Laibinis
Tuesday Morning, April 1, 1997
Nob Hill C

8:30 AM V3.1

COMPUTER SIMULATION OF THE PHASE BEHAVIOR OF SELF-ASSEMBLED MONOLAYERS, Alexander Pertain, Inst of Organic-Element Compounds, Moscow, RUSSIA; Michael Grunze, Univ of Heidelberg, Dept of Physical Chemistry, Heidelberg, GERMANY.

The phase behavior of self-assembled monolayers (SAMs) formed by long-chain functionalized molecules on the surface of solid substrates is simulated using two simple generalized models. One model deals with one-center particles representing molecular headgroups and treats the interaction of molecular chains in an implicit way, in terms of an effective potential for the headgroup-headgroup interactions. In the other model, the interactions of the chains are described explicitly, using an orientation-dependent anisotropic potential. Both models include a surface corrugation potential responsible for the headgroup-substrate interaction. The form and parameters of the model potentials are chosen so as to mimic the interactions in alkanethiol/Au(111) SAMs. The phase behavior of the model systems is explored using the Monte Carlo (MC) technique as a function of temperature, coverage, and the magnitude of surface corrugation. Aside from melting, both models predict a continuous commensurate-incommensurate solid-phase premelting transition. The transition involves coexistence of commensurate and incommensurate regions and provides a reasonable explanation for grazing incidence X-ray diffraction data by Fenter et al. (Phys. Rev. Lett. 1993, 70, 2447). At low coverages, the two-center model shows an interesting two-phase coexistence state. One of the phases represents a usual commensurate solid constituted by molecules with normal tilt angles. The other phase is liquid-like and characterized by anomalously large tilts of its constituent molecules. If the headgroup interactions are complemented with a Morse potential describing a disulfide bond, the two-center molecules can be packed into a stable "striped" phase, which involves linear head-to-head dimers lying in the surface plane and stacked into strips. Because of ergodic problems, however, the associated region in phase space cannot be reached in MC runs starting from normal monolayer configurations.

8:45 AM V3.2

THERMAL PHASE BEHAVIOR OF LONG CHAIN N-ALKANE AG THIOLATES: A VIBRATIONAL SPECTROSCOPY STUDY, Geoffrey F. Strouse, Susan D. Gillmor, Atul N. Parikh, Los Alamos National Laboratory, Dept of Chem Science & Technology, Los Alamos, NM; Thomas A. Zawodzinski, Los Alamos National Laboratory, Dept of Matls Science & Technology, Los Alamos, NM; Basil I. Swanson, Los Alamos National Laboratory, Dept of Chem Science & Technology, Los Alamos, NM.

Long-chain n-alkane substituted, silverthiolates bear a strong structural and geometrical analogy to a class of alkanethiol monolayers on Ag surfaces. The former also provides an example of layered, crystalline organo-inorganic materials. The phase behavior of the aliphatic chains in the above classes of materials is expected to be controlled by a presence of a covalent bonded, rigid inorganic (Ag) planes. We report temperature dependent, phase behavior for a self-consistent series of silver n-alkanethiolates using quantitative applications of infrared and Raman spectroscopies. A comparison of the observed phase behavior with that in correspondent monolayers

and related classes of organo-inorganic composites, e.g., alkyl zirconium phosphonates and biological membranes will be given.

9:00 AM V3.3

TBD.

(Abstract Not Available)

9:15 AM V3.4

ALKANETHIOLATE MONOLAYERS ON GOLD BEARING SUB-MONOLAYER COVERAGES OF SILVER, Paul E. Laibinis, G Kane Jennings, MIT, Dept of Chem Engr, Cambridge, MA.

Alkanethiols spontaneously adsorb onto an underpotentially deposited (UPD) layer of silver on gold to form a densely packed oriented film. The resulting three component systems have well-defined structures that are controllable at the atomic level through the use of electrochemistry and selection of adsorbate. These layered systems comprise an oriented organic self-assembled monolayer (SAM) that is chemically bonded to an epitaxial monolayer of silver atop a gold surface. The UPD metal adlayer influences the structure of the adsorbate, its packing density, its stability, and the nature of the chemical interaction present at the metal/organic interface. The described methods provide a direct nanoscale approach to modify the properties of SAMs (and inorganic/organic interfaces in general) and a convenient inroad for the synthesis that are not available by other means.

9:30 AM V3.5

SELF-ASSEMBLY IN THREE-DIMENSIONS: PREPARATION AND CHARACTERIZATION OF LAYERED, ORGANO-INORGANIC MICRO-CRYSTALLITES OF LONG-CHAIN, ALKYL POLYSILOXANES AND SILVER THIOLATES, Thomas A. Zawodzinski, Los Alamos National Laboratory, Dept of Matls Science & Technology, Los Alamos, NM; Atul N. Parikh, Susan D. Gillmor, Los Alamos National Laboratory, Dept of Chem Science & Technology, Los Alamos, NM; Basil I. Swanson, Los Alamos National Laboratory, CST-1, Los Alamos, NM.

Long alkyl chain substituted silver thiolates and polysiloxanes under suitable preparative conditions self-assemble into highly organized, layered, organo-inorganic materials. Here, we report the details of the molecular structure in the above two classes of materials deduced using a combination of spectroscopic, diffraction, and thermal analysis measurements. The cumulative evidence of the data show the structures to consist of highly uniform, double-layered micro-crystallites wherein the inorganic moieties, viz., silver and SiO_x, are present in periodic rigid backbones, separated by laterally organized assemblies of all-trans alkyl chains packed in a dense, crystalline habit. A comparison with correspondent substrate supported, single monolayers shows an existence of a strong structural analogy between the two structures. Implication of the above findings for the monolayer self-assembly mechanisms, specifically the relative roles of the interfacial ordering of the inorganic backbones and the ordering of the aliphatic chain matrix, will be discussed.

10:15 AM V3.6

LANGMUIR-BLODGETT ANALOGS OF LAYERED TRANSITION METAL PHOSPHONATES: MAGNETIC MONOLAYERS AND "DUAL-NETWORK" ASSEMBLIES, Daniel R. Talham, Gail E. Fanucci, Melissa A. Petrusek, Candace T. Seip, Univ of Florida, Dept of Chemistry, Gainesville, FL; Garrett E. Granroth, Mark W. Meisel, Univ of Florida, Dept of Physics, Gainesville, FL.

Known for most of this century, the Langmuir-Blodgett (LB) method is perhaps the earliest technique to afford molecular level control over the dimensions of supramolecular assemblies. However, many potential applications have not been realized because of the metastable nature of the layered organic assemblies. In particular, the demonstration of physical properties that require long-range structural order, such as superconductivity or magnetic order, has been elusive. We have recently developed a method for introducing long-range two-dimensional structural order into LB films. By taking advantage of the inorganic lattice energy of known solid-state layered structures, we have incorporated inorganic extended lattice structures into the hydrophilic portion of LB assemblies. In addition to adding structural order to the film, this approach provides the opportunity to introduce physical properties normally associated with inorganic extended lattice structures. As a demonstration of this concept, we recently characterized a magnetic LB film. This is the first example of cooperative magnetic ordering in an LB film. In this presentation, a series of Langmuir Blodgett film analogs of solid-state transition metal organophosphonates will be described. Complete structural characterization will be presented, including analyses by FTIR, XPS, ellipsometry, x-ray diffraction and EPR. In addition, the properties of the magnetic LB films will be compared with those of the isostructural bulk solids. Finally, attempts to include functionalized organic

molecules into the metal phosphonate LB systems will be presented. The objective is to prepare dual network assemblies, where both the organic and inorganic components add function to the LB films.

10:45 AM *V3.7

THE STEPWISE ASSEMBLY OF NANOCOMPOSITE THIN FILMS, Elaine R. Kleinfeld, Gregory S. Ferguson, Lehigh Univ, Dept of Chemistry, Bethlehem, PA.

The assembly of molecules as intact constituents to form larger, more complex structures has led to recent advances in the preparation of thin films and extended solids. We have developed a chemical method for the stepwise preparation of ordered multilayers by sequential adsorption of two components—a cationic polymer and an anionic sheet-silicate mineral—from aqueous solution or suspension onto various surfaces. These films are sufficiently ordered in the direction normal to the substrate surface to diffract x-rays, and have lattice spacings of nanometer dimensions. This talk will focus on the synthesis of these multilayers, analysis of their composition and structure, and studies of their properties. Particular attention will be given to new design principles developed in the course of these studies.

11:15 AM V3.8

USING SMALL ELECTROLYTES TO ALTER THE DEPOSITION OF IONIC MULTILAYERS TEMPLATED BY PATTERNED SELF-ASSEMBLED MONOLAYERS (SAMS), Sarah L. Clark, Martha J. Montague, Paula T. Hammond, MIT, Dept of Chemical Engr, Cambridge, MA.

Small cations and anions have unusual effects on the solubility properties of polyethylene glycol (PEG) [1]. For some electrolytes, PEG exhibits typical salting-out behavior in aqueous solutions, while for others, the PEG-complexed cation and the anion in the bulk solution enhance PEG solubility and structure. We utilize cations (Na^+ , Li^+ and anions (Cl^- and SO_4^{2-}) to enhance or destroy the adsorption resistance of a patterned PEG-terminated self-assembled monolayer (SAM). Micron-sized patterned surfaces of PEG and acid (COOH)-terminated SAMs on gold allow us to template the adsorption of ionic multilayers of polydiallyldimethylammonium chloride (PDAC) and sulfonated polystyrene (SPS) onto the acid regions. The ionic species effect on the PEG regions, paired with a competition between ions and the polyelectrolytes for the ionized acid surface, reverses the selective adsorption of the two regions as a function of electrolyte concentration in the solution from which the polyelectrolyte is adsorbed. This level of control over surface adsorption, combined with the supramolecular control of the ionic multilayer technique, has potentially promising applications for fabricating unique supramolecular waveguides, sensors, and other devices.

[1] Bailey F.E., R.W. Callard, *J. Applied Polym. Sci.* 1, 55-62 (1959).

11:30 AM V3.9

SEGMENTALLY FLUORINATED SELF-ASSEMBLED MONOLAYER FILMS ON GOLD, T. Randall Lee, Univ of Houston, Dept of Chemistry, Houston, TX; Hyun I. Kim, Thomas Kioni, Yasuhiro P. Miura, Scott S. Perry, Univ of Houston, Dept of Chemistry, Houston, TX.

Fluorinated materials play important roles in a variety of interfacial applications because (1) they are chemically and biologically inert, (2) they exhibit high thermal and mechanical stabilities, (3) they are resistant to oxidation and corrosion, and (4) they are water-resistant and nonadhesive. Our research outlines a systematic exploration of the molecular basis for wetting, adhesion, and friction in fluorinated thin films. The experimental approach relies on the construction of hybrid inorganic/organic interfaces composed of fluorocarbon/hydrocarbon overlayers. These composite films can be generated by the self assembly of segmentally fluorinated alkanethiols on gold. Studies of wettability and measurements of friction by atomic force microscopy will be presented.

SESSION V4: HETEROGENEOUS INORGANIC-POLYMER COMPOSITES

Chair: T. Randall Lee

Tuesday Afternoon, April 1, 1997
Nob Hill C

1:30 PM *V4.1

INTERFACE STRUCTURE AND DYNAMICS IN POLYMER NANOCOMPOSITES, Emmanuel P. Giannelis, Cornell Univ, Dept of MS&E, Ithaca, NY.

Composites with dimensions in the range of 1 nm to 100 nm, so-called nanocomposites, are the subject of intense current research and development. This activity stems from the markedly improved mechanical, barrier, swelling, and thermal properties of the

nanocomposites compared to the conventionally reinforced systems. In this talk I will review the strategies to synthesize various thermoplastic, thermosetting and elastomeric nanocomposites, present their properties, and discuss their potential applications. Emphasis will be placed on our recent understanding of the structure and dynamics of the nanocomposites and their effect on global, macroscopic properties.

2:00 PM *V4.2

HIGHLY ORIENTED LAYERED ORGANOCLEY NANOCOMPOSITES FROM HIGH TEMPERATURE ENGINEERING THERMOPLASTICS, Mark W. Ellsworth, Raychem Corp, Research & Development, Menlo Park, CA.

Highly oriented layered inorganic/organic nanocomposites have been produced by the intercalation of monomers and polymers into the galleries of surfactant modified layered clays using solvent-polymerization routes and, more recently, by conventional melt processing. The high aspect ratio and efficient dispersion of the surfactant modified clay results in a tremendous reinforcing effect at relatively low volume loadings. In addition to the reinforcing effect, these organoclay fillers also provide materials with unique barrier properties. Depending on the organoclay loading and polymer type, the water vapor permeability of a polymer matrix can be reduced by greater than 75%. The ability to achieve these highly dispersed, highly oriented morphologies, and the resulting property enhancements, by conventional melt processing is an important advancement in the development of applications for these materials. One important limitation of the melt processing approach is the thermal stability of the surfactant used to modify the clay layers. Previous research in this area has focused exclusively on alkylammonium modified layered clays. These organoclays are typically only stable up to 250°C. In order to produce nanocomposites using high temperature fluoropolymers and other engineering thermoplastics such as poly(ether ether ketones) and poly(imides) by conventional melt processing, more thermally stable organoclays have been synthesized from a variety of alternative surfactants. Surfactant modified layered clays which are stable at melt processing temperatures as high as 350°C have been used to produce composites from a variety of fluoropolymers and engineering thermoplastics. More importantly, the same highly dispersed, highly oriented morphologies are obtained with the high temperature polymers as are observed with the alkylammonium modified clays used with lower processing temperature polymers.

2:30 PM *V4.3

DNA-BASED METHODOLOGY FOR RATIONALLY ORGANIZING NANOPARTICLES INTO ORDERED AGGREGATE STRUCTURES, R. C. Mucic, J. S. Storchoff, R. Elghariani, R. L. Letsinger, Chad A. Mirkin, Northwestern Univ, Dept of Chemistry, Evanston, IL.

(Abstract Not Available)

3:30 PM *V4.4

H-2 AND Li-7 SOLID-STATE NMR STUDIES OF CONDUCTING POLYMER/OXIDE NANOCOMPOSITES, Linda P. Nazzari, William P. Power, Gillian R. Goward, Univ of Waterloo, Dept of Chemistry, Waterloo, CANADA.

We are interested in the structure and properties of conductive polymer/transition metal oxide nanocomposites. These are comprised of conductive organic polymers, such as poly(aniline) (PANI), interleaved between the layers of an inorganic oxide lattice, and are intriguing candidates for electrochemical applications. While the materials demonstrate interesting bulk properties, little is understood about the microscopic interplay between the polymer and the oxide, although several NMR studies have begun to provide details about the local structure of polymer and cations within the lattice. The primary concern addressed here is that of the interaction between the polymer and the oxide. What is the role of the polymer, how is it ordered, and does that order affect the electrochemical response of the system? H-2 and Li-7 NMR studies of solid polymer/oxide nanocomposites have been used to elucidate the structure and dynamics of polymers and charge-transport cations within these materials. H-2 NMR studies of oriented samples of $(\text{PANI})_{0.34}\text{MoO}_3$ provide evidence of preferential order of poly(aniline) within the MoO_3 lattice, and show that order is not determined solely by the oxide layers but manifested by the polymer between the layers as well. The polymer resides within the layers of MoO_3 with the plane of the phenyl rings within a Gaussian distribution of width 20° about the normal to the oxide layers. In contrast, poly(aniline) shows no such orientational order within other inorganic oxide hosts, i.e., V_2O_5 -xerogel or HWTaWO_6 . The oxide layers of all the materials impede the motion of the phenyl rings at elevated temperatures in comparison to pure poly(aniline). The influence of the polymer on cation structure is also manifested in the changes in Li-7 NMR line shapes followed as a function of

temperature. PANI appears to have little influence on chemically-inserted lithium ions, while PPY (poly(pyrrole)) changes the dynamics and local structure of the lithium sinks substantially

4:00 PM V4.5

A VISIBLE LED FABRICATED ON POROUS SILICON USING A POLYANILINE CONTACT, D. P. Halliday, J. M. Eggleston, P. N. Adams, A. P. Monkman, Univ of Durham, Dept of Physics, Durham, UNITED KINGDOM.

We have fabricated 20 mm diameter porous silicon wafers on (111) oriented n-type substrates with a resistivity of 10 Ωcm using electrochemical anodization in HF. A layer of p-type conducting polyaniline was deposited onto the porous silicon by spinning on a solution of polyaniline with Camphor Sulphonic Acid and Metacresole. The IV characteristics of the device show rectifying behavior with a rectification ratio of 490 at ± 5 volts. The data can be fitted to a simple Schottky type model giving a barrier height of 0.8 eV. The p-type polyaniline film has a transmission window between 800 - 600 nm. We have observed room temperature photoluminescence emission from the coated porous silicon layer which shows a peak at 600 nm with a FWHM of 170 nm. When a forward bias is applied to the junction with a current density of 0.5 A cm^{-2} , visible electroluminescence is observed with a peak at 790 nm and a FWHM of 270 nm. The efficiency is around 10^{-4} . Mechanisms of charge transfer between the polymer and the semiconductor and the effect of the interface characteristics on device performance are discussed.

4:15 PM V4.6

SYNTHESIS OF PbS NANOCCLUSERS WITHIN BLOCK COPOLYMER NANOREACTORS, Ravindra S. Kane, Robert E. Cohen, MIT, Dept of Chemical Engr, Cambridge, MA; Robert Silbey, MIT, Dept of Chemistry, Cambridge, MA.

We have demonstrated the synthesis of PbS nanoclusters within the microphase-separated films of diblock copolymers containing carboxylic acid units on one of the blocks. Lead was selectively sequestered into the acid-containing domains by treating the polymer films with tetraethyllead, and PbS was formed by subsequently treating the films with H_2S . The composite films containing PbS nanoclusters were characterized by x-ray diffraction, x-ray fluorescence, electron microscopy, and UV-vis spectroscopy. The nanocluster size could be controlled by varying processing parameters such as temperature, the presence of coordinating bases, and the H_2S exposure time. Increasing the size of the nanoreactors increased the cluster size. The universal cluster synthesis scheme enabled multiple passes through the process, which were used to increase the cluster size, and which could in principle be used to passivate the surface of the PbS cluster or to produce mixed semiconductor clusters.

4:30 PM V4.7

STABILIZATION AND SELF-ORGANIZATION OF NANOPARTICLES BY POLYMERS, G. Carrot, J. G. Hilborn, Swiss Federal Inst of Technology, Dept of Materials Science, Lausanne, SWITZERLAND; J. C. Valmalette, J. Dutta, S. Scholz, H. Hofmann, Swiss Federal Inst of Technology, Dept of MS&E, Lausanne, SWITZERLAND.

Composites based on particle-polymer matrix show interesting properties which could lead to potential switching application in electrical and optical devices. These properties are dependent on particle sizes and show strong non-linearities in the quantum size domains. In order to use these effects, it is necessary to control the size and the size distribution as well as the stability of the particle against agglomeration. Our approach consists of exploiting the possibilities arising from the use of graft copolymers obtained by macromonomer method. The ability of these copolymers to form stable micelles in selective solvent, has been checked by ^1H NMR spectroscopy. Micelles help to restrict the growth of the metal particles either by limiting the amount of metal particle precursor accessible to a growing nucleus or by restricting the motion of the growing nuclei, thus reducing the rate of productive collisions. Moreover, by using special monomers, like acrylic acid, it is possible to bind the metal particles onto the graft copolymer so as to reduce the migration of particles between the neighboring microdomains. Well dispersed particles less than 2 nanometers have been prepared and observed by transmission electron microscopy (TEM). The influence of the interparticle distance and the type of the interactions of the polymer with the particle (direct binding or complex formation) on the optical properties of the system is being studied.

4:45 PM V4.8

HETEROSUPRAMOLECULAR CHEMISTRY: THE SELF-ASSEMBLY AND SELF-ORGANIZATION OF NANOSTRUCTURES, L. Cusack, A. Gorelov, X. Marguerettaz, N. Rao, R. Rizza, J. Wenger, Donald Fitzmaurice, Univ College Dublin, Dept of Chemistry, Dublin, IRELAND.

Recent years have seen the development of powerful techniques and methodologies for the self-assembly and self-organization of supermolecules and for the preparation of metal and semiconductor nanocrystallites. Together, these developments allow us explore the possibility of self-assembling and self-organizing complex structures containing both molecules and nanocrystallites, referred to as heterosupramolecules. This talk will describe the self-assembly of a heterosupramolecular electron donor-acceptor complex in solution from a surface modified semiconductor nanocrystallite that can recognize and selectively bind, by complementary hydrogen bonding, an appropriately modified molecular acceptor in solution. Band-gap excitation of the semiconductor nanocrystallite results in electron transfer to the acceptor in the heterosupramolecule. Also described will be the extension of these studies to permit the self-assembly in solution of two semiconductor nanocrystallites, again by complementary hydrogen bonding, and their subsequent self-organization to form an ordered nanocrystallite array, or superlattice. Finally, our most recent studies directed toward the self assembly and self-organization of mixed metal and semiconductor nanocrystallite superlattices will be described.

SESSION V5: POSTER SESSION: INTERFACIAL EFFECTS AND ORGANIZATION OF INORGANIC-ORGANIC COMPOSITES

Chair: Paul E. Laibinis
Tuesday Evening, April 1, 1997
8:00 P.M.
Salon 7

V5.1

A SELF-ASSEMBLY APPROACH TO MOLECULARLY ENGINEERED TITANIUM SURFACES: APPLICATIONS TOWARDS SELECTIVE PHOTO-OXIDATION, Geoffrey F. Strouse, Sabina Johnson, Xiaoguang Yang, Atul N. Parikh, Basil I. Swanson, Los Alamos National Laboratory, Dept of Chem Science & Technology, Los Alamos, NM.

Engineering of metal surfaces through molecular self-assembly technologies is critical to the development of novel devices. We present recent data on the surface modification of titanium through the use of a patterned, self-assembly approach. The latter approach is shown to afford control over surface density and lateral distribution. By modifying the surface with molecular recognition components and photo-active materials, we demonstrate the applicability of selective photo-oxidation.

V5.2

ORGANIC-INORGANIC MOLECULAR HYBRIDS THROUGH HYDROGEN BONDING, Yoshiki Chujo, Kyoto Univ, Dept of Polymer Chemistry, Kyoto, JAPAN

This paper describes organic polymer hybrids with silica gels by means of sol-gel method. The incorporation of organic polymers at the level of molecular dispersion into metal oxide matrix was accomplished by the hydrolysis-condensation of tetraalkoxysilane (orthoasilate ester) in the presence of appropriate organic polymer. Especially, organic polymers consisting of amide groups such as poly(2-methyl-2-oxazoline) were found to form molecular hybrids with silica gel through strong hydrogen-bondings. The organic-inorganic polymer hybrids obtained were homogeneous and transparent glassy composite materials in a wide range of the contents of organic polymers. The homogeneity of the hybrid may be due to the molecular dispersion of organic polymer in the silica gel matrix, which is ascribed to the hydrogen-bonding formation between the polymer amide group and silanol group of silica gel. The hydrogen-bond was actually supported by FT-IR spectra of hybrids. Another interesting material is porous silica gel having controlled size pores which is prepared by the pyrolysis of the hybrid at a temperature far below the fusing point of silica gel.

V5.3

Abstract Withdrawn.

V5.4

POLYACETYLENE IN NANO-STRUCTURED INTERCALATION COMPOUND, Motoki Kaneno, S. Yamaguchi, K. Nakayama, Taro Eguchi, Nobuo Nakamura, Osaka Univ, Dept of Chemistry, Toyonaka Osaka, JAPAN; Koichi Niihara, Osaka Univ, Inst of Scientific & Industrial Res, Osaka, JAPAN.

On the basis of our guideline regarding a guest molecule in intercalation compound, we designed and synthesized the molecule with diacetylene group. The diacetylene derivative was readily intercalated into gamma titanium phosphate. Polymerization of the

diacetylene derivative in the intercalation compound was attempted by several methods. We will discuss the characterization and physical properties of the polymerized intercalation compound.

V5.5

PREPARATION OF SPHERICAL FINE ALUMINA PARTICLES WITH USE OF VESICLES, Chang-Hyun Kim, Kaya Univ, Dept of Elect Ceramics Engrg, Kyungpook, SOUTH KOREA; Chang-Seop Ri, Taegu, SOUTH KOREA.

The precipitation of small (ca. 50 nm) Al_2O_3 crystallites within unilamellar vesicles has been studied by transmission electron microscopy. Precipitation started at pH of 11.0 and optimal precipitation condition of pH was 12.0. Above pH of 12.0, size of precipitates grew twice as those below 12.0 due to agglomeration and coalescence with time. In order to analyze and investigate the effects of heat treatment of aluminum precipitate produced within vesicles, heat treatment was conducted in various temperatures: 100°C, 500°C, 900°C, and 1100°C. Phosphatidylcholine constructing vesicle was polymerized at 120°C and did thermal behavior up to 900°C. Owing to the maintenance of thermal behavior of phosphatidylcholine in high temperature, mass transfer between the precipitates in vesicles was removed. Therefore, agglomeration of particles while α -alumina phase was synthesized from transition phase restricted and monodispersed spherical fine alumina powders with the about 50 nm primary particle size were prepared.

V5.6

ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL PROPERTIES OF α - Fe_2O_3 NANOMETER PARTICLES, Maizhi Yang, Uppsala Univ, Dept of Physical Chemistry, Uppsala, SWEDEN; Wen Zhang, Shengmin Cai, Peking Univ, Dept of Chemistry, Beijing, CHINA.

The semiconductor ultrafine particles (UFP), ranging in size from 1 nm to almost 100 nm, i. e., species representing the neglected dimension between single atoms or molecules and bulk materials, behave physical and chemical properties different from both bulk material and the molecule or atom composing them. Usually, the size quantization effect and the big ratio of area/volume for UFP are well known, but few people think of the dielectric confinement effect produced by the environment of small dielectric constants^[1,2]. In our work, we prepared α - Fe_2O_3 nanometer particles coated with a layer of steric acid (ST) molecules by phase transfer method. A significant red shift of optical absorption band edge was observed as the size of particles decreasing, which exhibits the dielectric confinement effect. The influence of dielectric confinement effect on electrochemical and photoelectrochemical properties of α - Fe_2O_3 UFP was investigated by cyclic voltamogram and photocurrent-potential graphs. Comparison between the CV graphs of naked and coated α - Fe_2O_3 UFP suggests that the ST coating layer with small dielectric constant (1.2) decreases the shield of electric force line, which is favored for charge transfer on the surface of UFP. The photoelectrochemical results showed that the dielectric confinement effect of coating layer influences the photoelectrochemical behavior of α - Fe_2O_3 UFP.
[1] B.L. Ye, etc., Acta Phys. Chem. Sinica, 1994: 10 (2) 103
[2] T. Takagahara, Phys. Rev. B., 1993: 47, 4569.

V5.7

SELECTIVE ALDEHYDE-ABSORPTION WITH INTERCALATION COMPOUND OF LAYERED PHOSPHATE, Motoki Kaneno, Osaka Univ, Dept of Chemistry, Toyonaka Osaka, JAPAN; Shunro Yamaguchi, Osaka Univ, ISIR, Osaka, JAPAN; Hirokazu Nakayama, Taro Eguchi, Nobuo Nakamura, Osaka Univ, Dept of Chemistry, Osaka, JAPAN.

We synthesized polyamine-zirconium phosphate intercalation compounds and examined the inclusion property of the obtained intercalation compounds for aldehydes. Aldehyde with alpha-hydrogen was absorbed in the intercalation compound; however, aldehyde without alpha-hydrogen was not absorbed. From solid state NMR, it was confirmed that the aldehyde reacted with intercalated polyamine at terminal primary amino group. Polyamine-zirconium phosphate intercalation compounds possess enough spaces and reactive sites for the guest molecule between the inorganic layers, which serve as a selective aldehyde absorbent.

V5.8

PREPARATION OF LAYERED PEROVSKITE QUANTUM-WELL BY A SIMPLE DUAL SOURCE VAPOR DEPOSITION, Masanao Era, Y. Rikihisa, K. Maeda, T. Taira, T. Tautsui, Kyushu Univ, Dept of Matls Science & Technology, Kasuga-shi, JAPAN

Layered perovskites $(\text{RNH}_3)_2\text{MX}_4$ possess a quantum-well structure where a two-dimensional semiconductor layer of MX_4 (M: Pb, Sn, etc., X: Cl, Br, I) and an organic ammonium layer of RNH_3 , are alternately piled up. Owing to the low-dimensional semiconductor nature, the

perovskites form stable exciton with a large binding energy of several hundreds eV. Further, the perovskites have been found to exhibit attractive optical effects due to the exciton, for example, sharp and intense electroluminescence and high efficient optical nonlinear effect. In this study, oriented thin films of Pbi-based perovskites were found to be self-organizingly grown on fused quartz substrates by a simple dual source vapor deposition of lead iodide PbI_2 and an organic ammonium iodide RNH_3I . When PbI_2 and RNH_3I such as phenethylammonium iodide were evaporated and deposited simultaneously on fused quartz substrated under a pressure of about 10^{-6} torr, the vacuum deposited films showed strong exciton absorption at room temperature. The appearance of sharp exciton absorption and emission clearly demonstrated the formation of the layered perovskite quantum-well structure in the vacuum-deposited films. Further, the x-ray diffraction measurement on the vacuum-deposited films demonstrated that the layer structure of the vacuum-deposited film were oriented parallel to the film phase.

V5.9

SYNTHESIS OF SILICA-FURFURALDEHYDE COMPOSITE, Ruben Sanchez, Teresita Garcia, Ricardo Martinez, UENF, Dept of Polimeros, Rio de Janeiro, BRAZIL.

Furfuraldehyde is the most important of the first-generation derivatives obtained from wastes of the sugar-cane industry by simple acid-catalysed depolymerization and condensation reactions. Furfuraldehyde was polymerized in a suspension of dispersed silica in 1,2 dichloroethane using trifluoroacetic and sulfuric acids as initiators. The presence of silica allows that furfuraldehyde polymerization to take place on its surface while no polymerization is produced in the homogeneous liquid phase with the acid quantities employed. The grafted polymer determined by gravimetric method corresponded to a strongly reticulated structure. A morphological characterization was performed by Optical Microscopy (OM), Scanning Electron Microscopy (SEM), and Isothermal Nitrogen Adsorption (BET method). The composite turned into a yellow-golden color when trifluoroacetic was employed, and a black color when sulfuric acid is initiator, due to the structural differences between these composites. The composite particles observed by Optical Microscopy represented size ranging from 250 to 303 micrometers long and 207 to 266 micrometers wide. No agglutination of particles was observed and the texture of the silica surface was practically unchanged, pointing out that the polymerization process occurs in the surface of each independent particle. These results indicated that the organic phase in the sulfuric composite had a similar cross-linked structure to furfuraldehyde bulk resins, that it has a good adsorbate property and chemical stability, thus suggesting that the potential of this composite as reverse phase to liquid chromatography.

V5.10

TEM OBSERVATION OF METAL-OXIDE NANOPARTICLES DISPERSED IN MESOPOROUS-ACTIVATED CARBONS, Noriko Yoshizawa, Yoshio Yamada, Minoru Shirasahi, NIRE, Carbon Materials Lab, Tsukuba, JAPAN; Shigeyuki Kojima, Hisashi Kojima, Hajime Yasuda, Hiroshima Univ, Dept of Engr, Higashi-Hiroshima, JAPAN

Activated carbons having much amount of mesopores, expected for an adsorption process of macromolecules in liquid media, were prepared by steam oxidation of the mixture of coal and metal (Fe, Ni, Co) complex at 900°C. According to the BET and BJH analysis of N_2 adsorption isotherm at 77 K, all of the activated samples showed mesoporous textures even at an early stage of activation. Especially Fe and Co complex were effective to obtain exclusively mesoporous textures compared with the activated carbons without metal complex. X-ray diffraction (XRD) patterns indicated the presence of small graphite-like stacking structure, together with metal oxide crystallites corresponding the type of metals used for preparation (Fe_3O_4 , NiO and Ni_2O_3 , and CoO). Observation with transmission electron microscope (TEM) showed nano scale oxide particles homogeneously dispersed in the disordered carbon matrix. Resemblance in shape between characteristic mesopores and oxide particles were also confirmed. Particle size distribution determined by image analysis of TEM photograph suggested the similarities in the average sizes of the oxide particle and mesopores. From those results, formation of the mesoporosity in the activated carbon was closely related with the behavior of metals in the oxidation atmosphere, including migration or removal of metal oxide particles from carbon matrix.

V5.11

THE POROUS "ORGANIC POLYMER-METAL" COMPOSITE MATERIALS, Nikolay F. Yudanov, Galina N. Chekhova, Juri H. Krieger, Valentin N. Mitkin, Inst of Inorganic Chemistry, Novosibirsk, RUSSIA

Composites consisting of organic polymeric matrixes and of metal particles 50A in size are prepared by thermal decomposition of

carboxylic acids salts. As the size and the form of particles of composites correspond to those for initial salts, the removal of carbon dioxide at thermal decomposition provides to formation of open pores. Due to high porosity of composites the metal and the matrix both are accessible for chemical effect of gases and liquids. The chemical structure and the properties of composites can easily be changed by their chemical treating. So the composite containing approximately 70 weight % Cu and being dielectric, after treating by hydrogen sulphide has low specific resistance. The fluorination of these composites results in formation of new composites, consisting of a metal fluoride and of a fluorinated matrix. It is necessary to note, that such chemical treating, as well as removal of metal do not result in change of the form of particles of a composite. Such composites can be used as novel sorbents, catalysts, membranes or as cathodic materials in lithium batteries. As these composites can be prepared in kind of thin films with high thermal stability (about 400 °C), their use in electronics, in particular, in molecular electronics as well as for creation of sensor is obviously possible.

V5.12

A VERY COLD NEUTRONS INVESTIGATION OF SiO₂ NANOPARTICLES IN POLYMERS: SCATTERING FROM FRACTAL STRUCTURE AND CORRELATED STRUCTURE, Anatoliy A.D. Perekhrenko, Aleksey A. I. Isakov, Igor I. V. Meshkov, Sergey S.P. Kuznetsov, Lebedev Physics Inst, Moscow, RUSSIA; Anatoliy A. V. Shelagin, Dmitriy D. A. Shelagin, Moscow Physical & Tech Inst, Dolgoprudnyi, RUSSIA; Lyudmila L. A. Novokhonorova, Vadim V. G. Kraheninnikov, Semenov Inst of Chemical Physics, Moscow, RUSSIA.

It is well known that SiO₂ nanoparticles aggregate in fractal-like structures in polymer/inorganic composites. X-rays and thermal neutrons small angle scattering are the usual methods to study the similar structures. In this paper, the scattering of very cold neutrons (VCN) in the wavelength region from ones to hundreds nanometers have been suggested as a new method to investigate the fractal structures. It has been shown theoretically that the fractal dimension, fractal particle size, as well as fractal domain size determine the VCN scattering cross section. The VCN scattering by ordered fractal-like structures depends on superlattice parameters and ordered domain sizes. The Aerosil/polyethylene composite with 1.5% and 11.5% SiO₂ nanoparticles concentrations have been investigated by VCN time-of-flight spectrometer in VCN transmission experiments. Data analysis give us the possibility to conclude that SiO₂ particles having 9 nm-radius aggregates in dense ordered hexagonal structure with superlattice parameters, $a = 18$ nm, $c = 29$ nm, and ordered domain size, 400 nm.

V5.13

CHELATING MONOMERS AS SURFACTANTS IN TRANSITION METAL BASED ORGANIC-INORGANIC COMPOSITE MATERIALS, Martin S. In, CNRS, Complex Fluid Laboratory, Cranbury, NJ; Clement Sanchez, Univ Pierre et Marie Curie, Chimie de la Matière Condensée, Paris, FRANCE.

Hydrolysis and condensation equilibria involved in sol-gel chemistry have been treated as competitive adsorption isotherms of various kinds of mineral and organic ligands. This allows us to establish the affinity order of these ligands for the coordination sphere of the metal: $PCL > O > OH > OR$, where OR, OH and O are respectively alkoxo, hydroxo and oxo ligands and PCL is a chelating monomer. This order validates the principle of synthesis of transition metal based hybrid organic-inorganic copolymers from heterofunctional precursor $M(OR)_n-x(PCL)_x$. The copolymers obtained from the double polymerisation of such an heterofunctional precursor, for instance $Zr(OPr)_3(AAEM)$, have been characterized by chemical analyses, various spectroscopies (UV, NMR, IR) and by high resolution small angle X-ray scattering. Competition between the two types of polymerisation has clearly been demonstrated. It can be arbitrated through the parameter x . The main issue of this competition is the heterogeneity scale inside the composite network. In other words, the extent of interface between organic and inorganic moieties is determined at the precursor level by the parameter x . The chelating monomer can thus be regarded as a surface acting agent reducing the interfacial tension between organic and inorganic phases.

V5.14

DYEING DOPED FERROELECTRIC CRYSTALS FOR OPTICAL APPLICATIONS, Janardhanan A. Subramony, Bart E. Kahr, Purdue Univ, Dept of Chemistry, West Lafayette, IN.

A variety of inorganic matrices can encapsulate organic dye molecules; some of the resulting hybrid materials have been proposed and tested for optical applications. Thus, recent literature has featured photophysical studies of dyes captured within the pores of sol-gel glasses, threaded through channels of zeolites, or sandwiched between the layers of clays, semiconductors, and codeposited salts. Here, we

introduce another type of organic/inorganic hybrid material based on simple ionic, inorganic salts, that do not have preformed layers, channels or pores, but have nevertheless adsorbed, oriented, and overgrown dyes during growth from solution. These are prototypical materials for studying the photophysical perturbations of inorganic hosts upon organic guest. Herein, we emphasize the growth and optical characterization of organic dyes encapsulated within ferroelectric crystals such as KDP. Fluorescent dyes ordered by host crystals with large second-order nonlinear susceptibilities might ultimately function as compact self-frequency doubled single crystal dye lasers. We report the results of polarization spectroscopy, modeling of the inclusion process, fluorescence lifetime measurements upon passing through the Curie point, atomic force microscopy, and dielectric measurements. We speculate on the potential role of KDP dye inclusion crystals as novel photorefractive or electroluminescent materials.

V5.15

COATING AND REACTIONS OF TEOS/VTES SOL-GEL SOLUTION, Young-Joo Eo, Sang-Soo Han, Duk-Jun Kim, Byeong-Soo Bae, KAIST, Dept of MS&E, Taejeon, SOUTH KOREA; Ki-Chang Song, Keun-Yang Univ, Dept of Chemical Engr, Chungnam, SOUTH KOREA; Seung-Won Song, Kwang-Sik Chung, Taedok Inst of Technology, Taejeon, SOUTH KOREA.

Inorganic-organic hybrid materials can be used for glass and plastic coating. There are many applications such as photochromic coating, color coating, dust repellent coating, antifogging coating, etc. In this study, the reactions in TEOS/VTES solution which can be used as a functional coating on plastic, has been studied. The solution is coated on glass and polymer substrates. Optical microscope, SEM (scanning electron microscope) is used to observe the surface morphology, and the reactions among the alkoxide are examined by liquid state ²⁹Si nuclear magnetic resonance (NMR) spectroscopy. The morphology of the coating is dependent upon chemical composition and processing parameters and exhibit micropore with the diameter of which is about 5000 Å. Also the micropore in the coating is caused by phase separation with polymer rich phase and polymer lean phase. The phase separation region will be examined and optimum composition and condition for coating will be found.

V5.16

MORPHOLOGY AND BARRIER PROPERTY CORRELATION IN POLYMER/GRAPHITE COMPOSITES, Deanna N. Busick, North Carolina State Univ, Raleigh, NC; Richard J. Spontak, C. Maurice Balik, North Carolina State Univ, Dept of MS&E, Raleigh, NC.

While the diffusion of small molecules into an organic/inorganic composite can be of crucial importance in commercial applications, surprisingly few efforts have attempted to identify barrier property/morphology correlations in such materials. In this study, we have performed a series of systematic and coupled diffusion/morphology analyses to ascertain the existence and composition dependence of voids in polymer/graphite composites varying in graphite concentration as well as in processing. Sorption data for a probe gas (CO₂), collected by a conventional gravimetric method, obey the dual-mode sorption model and provide evidence that the void fraction increases with increasing graphite level. Environmental scanning electron microscopy (ESEM) has been employed here to elucidate the morphological characteristics of these composites. Stereological analysis of backscattered electron (BSE) images acquired from microtomed specimens reveals that the graphite percolation threshold can be identified in this fashion. At the onset of this threshold, graphite particles form a continuous pathway throughout the isotropic composite, thereby permitting the flow of electrical current. The composition range over which this threshold occurs is in good agreement with data collected from both sorption and resistivity measurements. Our results strongly suggest that the voids in this family of composites are associated with relatively poor adhesion along polymer-graphite interfaces, and that the voids are discrete (i.e., they do not form a continuous percolation network, even though the graphite particles do).

V5.17

THE ARAGONITE-HYDROXYAPATITE TRANSFORMATION IN ABALONE SHELL NACRE, Charlotte M. Zaremba, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA; Stephen Mann, Univ of Bath, Dept of Chemistry, Bath, UNITED KINGDOM; Daniel E. Morse, Univ of California-S Barbara, Dept of Biological Sciences, Santa Barbara, CA; Paul K. Hansma, Univ of California-S Barbara, Dept of Physics, Santa Barbara, CA; Galen D. Stucky, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA.

The nacre of the red abalone shell is a remarkably tough composite of single-crystal tablets of aragonite (CaCO₃) 0.4 µm thick and 5-10 µm wide, which are surrounded and interconnected by a 4 weight % biopolymer matrix. The tablets are arranged in columnar,

interdigitating stacks elongated normal to the shell surface, with the crystallographic *c* axis of the aragonite in the composite oriented normal to the shell surface. The transformation of this nacre from aragonite to hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ by hydrothermal ion exchange [1] has been studied to determine the structure-directing influence of an interpenetrating organic matrix on solid-state reactions and to create a potential biomedical material. Surprisingly, pieces of nacre remain intact after complete transformation, which takes place at temperatures above 140°C. Although the strength of the composite is reduced by the reaction, the tablet and column-of-tablets ultrastructural features are preserved. The hydroxyapatite-organic composite has a preferred crystallographic orientation derived from its aragonite nacre precursor. The effects of temperature and pressure on reaction kinetics and the ultrastructure, hardness, organic content, crystallographic orientation, and crystallinity of hydroxyapatite-converted nacre and a comparison between the transformation in *Porites* coral skeleton and geological aragonite with nacre will be presented.

[1] Roy D.M., Linnehan S. K., *Nature* 1974, 247, 220.

V5.18

MESOPOROUS MCM-48 SUPPORTED TRANSITION METALS AS FUNCTIONAL HALOPEROXIDASE BIOMIMICS AT NEUTRAL pH. Mark Sanson Morey, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA; Jerrylaine V. Walker, St. Jude Childrens Research Hospital, Dept of Molecular Pharmacology, Memphis, TN; Michael Froeba, Univ Hamburg, Inst of Inorganic & Applied Chem, Hamburg, GERMANY; Alison Butler, Galen D Stucky, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA.

Intense interest has been shown in the new class of silica-based, mesoporous materials due to their high potential as supports for catalytic applications. Of these materials, the cubic MCM-48 possesses a high surface area (1100-1500 m²/g), a 3-D array of pores, and a large pore diameter (20-100) so that selectivity for large (>10 kinetic diameter) molecules is possible. Here we use pure silica MCM-48 as a support for Ti, V, Zr, Mo, and W which are grafted via surface silanols. Bulk structural characterization by X-Ray powder diffraction and N₂ adsorption shows that the open pore structure is retained after grafting and no metal oxide clusters are formed. The local metal center environments and features such as the M-O-Si bond formation were studied by FTIR-PAS, UV/Vis and X-Ray absorption spectroscopy. These materials have been found to be active in the bromination of large organic substrates and are the first haloperoxidase biomimics which function at neutral pH. Characterization, comparative rate data and possible mechanisms will be discussed.

V5.19

TEMPERATURE INDUCED STRUCTURAL RECONSTRUCTIONS IN LAYERED, CRYSTALLINE POLY (N-ALKYLSILOXANES). Susan D. Gillmor, Atul N. Parikh, Los Alamos National Laboratory, Dept of Chem Science & Technology, Los Alamos, NM; Thomas A Zawodzinski, Los Alamos National Laboratory, Dept of Matls Science & Technology, Los Alamos, NM; Geoffrey F. Strouse, Basil I Swanson, Los Alamos National Laboratory, Dept of Chem Science & Technology, Los Alamos, NM.

The formation of highly organized, layered organo-inorganic microcrystallites of poly(alkyl)siloxanes by a simple hydrolytic condensation of trichlorosilyl precursors has been recently demonstrated. The microcrystallites are shown to be comprised of periodic arrays of inorganic siloxy backbones separated by conformationally ordered, aliphatic chains in a fixed orientation. In the present study, the thermal phase behavior of a self-consistent series of long-chain poly(alkyl)siloxanes has been investigated using infrared and Raman spectroscopies. The data show unique chain-length dependent, structural reconstructions in both the alkyl phase and the inorganic backbone structure. A comparison of these results with the phase properties of unsubstituted long-chain hydrocarbons provides an understanding of the influences of the siloxy backbone on chain-melting in a constrained molecular environment.

V5.20

SYNTHESIS, SURFACE CHARACTERIZATION AND CATALYTIC ACTIVITY OF ZIRCONIUM-DOPED MESOPOROUS SILICA. Pedro Maireles-Torres, Jose Jimenez-Jimenez, Pascual Olivera-Pastor, Enrique Rodriguez-Castellon, Antonio Jimenez-Lopez, Univ de Malaga, Dept de Quimica Inorganica, Cristalografia & Mineralogia, Malaga, SPAIN; Deborah Jones, Univ de Montpellier II, Lab des Agregats Moleculaires et Matls, Montpellier, FRANCE; Jacques Rosiere, Univ de Montpellier II, Lab des Agregats Moleculaires & Materiaux Inorganiques, Montpellier, FRANCE.

Zirconium containing mesoporous silica has been prepared from tetraethylorthosilicate and zirconium tetra n-propoxide using

hexadecyltrimethylammonium bromide as a template. Materials calcined at 540°C show a single, well defined diffraction line with *d*100 ranging from 33.5 Å (Si/Zr = 50) to 31.7 Å (Si/Zr = 25). The wall thickness of Si/Zr materials calculated using the average pore diameter and the *a*₀ parameter of the hexagonal unit cell is higher (12-16 Å) than that (10 Å) of the purely siliceous analog prepared under identical conditions. In transmission electron micrographs, a roughly hexagonal arrangement of pores is observed. Chemical analysis and XPS depth profiling indicate the Si/Zr ratio at the surface to be higher than that in the bulk, compatible with the more rapid hydrolysis of Zr alkoxides. Binding energies for Zr3d_{5/2} and O1s are closer to those of ZrSiO₄ than of ZrO₂, in favor of incorporation of Zr in the siliceous framework. Ir analysis following adsorption of pyridine onto the calcined materials shows the absence of Brønsted acid sites, and that the number of Lewis acid sites increases with the Zr content. Total acidity determined by ammonia-TPD follows the same trend. The sample with Si/Zr = 5 has a greater total acidity than MCM-41 aluminosilicates. Most relevant results were obtained using the decomposition of isopropyl alcohol as test reaction. Here, whereas the pure siliceous phase was inactive, calcined Si/Zr samples displayed 99% selectivity towards propene and high catalytic activity

V5.21

SURFACTANT-TEMPLATED SILICA AEROGELS. Mark T. Anderson, James E. Martin, Patti Sawyer, Sandia National Laboratories, Albuquerque, NM.

Aerogels are low density, high surface area materials that are formed by extracting the pore fluid from a wet gel. Aerogels generally have a broad, continuous distribution of pore sizes that range from microporous to macroporous exist within the material. Here we report a procedure to produce aerogels that have a set of unimodal mesopores with a very narrow pore size distribution in addition to macropores. To synthesize these periodic materials, we combine a molecular source of silica, tetramethoxysilane, with an alkaline micellar solution to form a physical gel monolith. The gel contains particles that range 50 to 500 nm; within each particle there is a hexagonal arrangement of tunable 1-d mesopores (15-50 Å) that contain liquid-crystalline-like surfactant assemblies. We exchange the aqueous pore fluid with alcohol and then with CO₂. The samples are extracted at the critical point of CO₂. The monoliths do not shrink during extraction as compared to a > 50% shrinkage when they are dried in air. The monoliths can be made with bulk densities less than 100 mg/cm³ and are opaque. We will discuss the effects of aging time and silica concentration on porosity and density. Substituted silicate frameworks have also been synthesized.

This work was funded by the United States Department of Energy under Contract Number DE-AC04-94AL85000

V5.22

SYNTHESIS OF CONTINUOUS SURFACTANT-TEMPLATED SILICA FILMS FROM HOMOGENEOUS ALCOHOLIC SOLS. R. Ganguli, Y. Lu, Univ of New Mexico, Albuquerque, NM; Mark T. Anderson, Sandia National Laboratories, Albuquerque, NM; C. J. Brinker, Univ of New Mexico, Albuquerque, NM; H. Soyez, M Huang, B. Dunn, J. I. Zink, Univ of California-Los Angeles, Los Angeles, CA.

Surfactant-templated films have potential applications as membranes, optically based sensors, and catalysts. Here we report a method to fabricate periodic mesostructured silica films from alcoholic surfactant/silica coating solutions. Films are produced by drawing nonporous substrates at a constant rate from the coating solutions. As the substrates are drawn, the alcohol preferentially evaporates, concentrating the solution in water, acid, silica, and surfactant. Templating at both the air-sol and substrate-sol interfaces affords regular, periodic mesostructures near the interfaces, as confirmed by x-ray diffraction and cross-sectional TEM. Owing to the rapid kinetics and induced compositional gradients, the center of the films exhibit disordered, transitional mesostructures that are stable to calcination. *In situ* fluorescence depolarization experiments confirm that the surfactant concentration in the initial sol is less than cmc, but that cmc is exceeded before the final film forms. Nitrogen sorption experiments on calcined films coated on surface acoustic wave devices show that the porosity is accessible and that the surface areas are greater than 1000 m²/g.

V5.23

CONTROLLED CRYSTALLIZATION OF CALCIUM PHOSPHATE FROM SOLUTION OF EQUAL CONCENTRATION OF Ca²⁺ AND Mg²⁺ UNDER STEARIC ACID MONOLAYER. Chunlai Ma, Feng Qian, Chi Zhang, Tsinghua Univ, Dept of MS&E, Beijing, CHINA.

To investigate the influence of some metallic ions on the controlled crystallization of calcium phosphate, the crystallization of calcium phosphate at 37°C from the solution of equal concentration of Ca²⁺ and Mg²⁺ ([Ca²⁺] = [Mg²⁺] = 4 mM) in the presence of stearic acid

monolayer was studied by scanning electron microscopy with EDX, transmission electron microscopy with selected-area diffraction and X ray diffraction. The pH value is around 7.0. No magnesium phosphate was found precipitate from the solution while the fashion of the crystallization of calcium phosphate is far different from in the system without Mg^{2+} in it. The first precipitating phase is almost an amorphous calcium phosphate which transforms into a mixture of oriented hydroxyapatite (HAP) and octacalcium phosphate (OCP). Subsequent growth results in oriented OCP tiny crystals while no more HAP grows, and some ball-like products which size vary according to the variation of pH value appear. Same study was carried out in the system which has no Mg^{2+} in it for the purpose of comparison. The role of Mg^{2+} in controlled crystallization was discussed.

V5.24
EFFECT OF LANGMUIR MONOLAYER COMPRESSION EXTENT ON THE INTERFACE COPPER IONS CLUSTERS FORMATION, Tatiana V. Yurova, Gennady B. Khomutov, Eugene S. Soldatov, Serge A. Yakovenko, Moscow State Univ, Dept of Biophysics, Moscow, RUSSIA.

Multicomponent organised molecular mono- and multilayer films with incorporated or grown nanoparticles are very promising material for nanotechnology and molecular electronics. The formation of such a films is faced with a problems of elucidation the role of organic surfaces to mediate inorganic crystallization at the interface and of development the methods to controllably manipulate the supramolecular assemblies. The effects of stearic acid monolayer compression extent on the interface copper ions binding and clusters formation have been studied in dependence on pH and ionic content of water subphase. Copper ions were added in to aqueous phase under different fixed monolayer compression extent and after equilibration (effective mixing of bulk phase was executed) the pressure-area isotherm changes and copper binding to monolayer were measured. STM study of monolayer LB films, deposited on pyrolytic graphite substrates, discovered nanosized (5 nm) clusters formation on monolayer surface. In pH region 5.2-6.0 (a little lower pH were metal hydroxide begins to precipitate) the enhance in monolayer stability and copper binding were observed, correlated with clusters formation. Copper binding and clusters formation strongly depended on monolayer compression extent and had sharp maximum at surface pressure about 20 mN/m. The data obtained showed that interaction of monolayer with copper ions and accompanying clusters formation processes are determined by arrangement, order and mobility of monolayer stearic acid molecules, electrostatics and pH at the interface.

V5.25
A THIN ORGANIC TEMPLATE FOR BIOMIMICKING HIGH PERFORMANCE CERAMICS, Necesio Costa, State Univ of Campinas, Fac of Mech Engr, Campinas, BRAZIL; Peter M. Marquis, Univ of Birmingham, School of Dentistry, Birmingham, UNITED KINGDOM.

Most ceramics for surgical implantation are better tolerated by the body environment than other biomaterials (e.g. Al_2O_3 , composite ceramics). However, their application is limited because they are brittle and prone to catastrophic failure. In contrast, ceramic biocomposites, organic and produced in nature, can possess adequate mechanical properties which make them suitable for use as biomaterials. An example would be the mollusc shell, where an inorganic phase grows onto a charged and organized organic template. This natural biomineralization provides a calcium carbonate phase with satisfactory properties, which would be suitable for surgical implantation. Langmuir Blodgett has been used as a organic template for calcium phosphate crystallization. Three different Langmuir Blodgett Films: ω tricosanoic acid, stearic acid and octadecylamine have been used. The Langmuir Blodgett Films obtained had methyl (CH_3), calcium carboxylate ($CaCOO$) and amine (NH_2) as functional groups. AFM and SEM results show that calcium phosphate crystallization occurs in a similar manner to natural biomineralization. The calcium carboxylate head group appears to have a physical influence on the size and shape of the calcium phosphate crystals. Under the experimental conditions tested, the calcium carboxylate functional head group controls calcium phosphate crystallization by a biomimetic approach. This study strongly suggests that the biomimetic approach has the potential for producing high performance ceramics comparable with those made by mollusc shells.

V5.26
INTERCALATED LAYERED SILICATE COMPLEXES: EXPERIMENTAL, AND MOLECULAR MODELING RESULTS, Gary W. Beall, Simeon J. Tsipursky, Don Eisehour, Nanocor, Inc., Arlington Heights, IL; Cynthia Harwood, Molecular Simulations, Naperville, IL.

The intercalation of clay layered silicates (Na-montmorillonite) with different organic molecules is an important process in making polymer nanophase composites. A new family of intercalated clays have been produced and characterized. Using x-ray diffraction and TGA analysis complexes intercalated with caprolactam, γ -butyrolacton, 2 pyrrolidone, n-alkylpyrrolidone, and n-ethylhydroxypyrrolidone were studied. These data allowed the elucidation of the mechanism of intercalation. To understand the behavior of solvent molecules on the surface of montmorillonite, the computational chemistry program Cyrius² was applied. All minimizations were performed using the Universal Force Field together with the Minimizer and Dynamics modules in the Cyrius² software package. The optimum montmorillonite structure, gallery spacing, and molecular arrangements in intercalated complexes were calculated by changing interlayer spaces and reoptimizing the positions of the sodium cations, waters, and solvents until the minimum energy was obtained. Experiments and computational calculations revealed several fundamental principles that control the process of intercalation. Thus, the value of molecular dipole moment is one of the most important parameters which drives the molecule to intercalate the montmorillonite. Calculations yielded steric configurations of solvent molecules around sodium cations on the surface of montmorillonite and their organization within gallery. Good agreements in sizes of interlayer spaces of intercalated montmorillonites were obtained between x-ray powder diffraction experimental data and calculated structural parameters.

V5.27
SURFACE-INDUCED POLYMERIZATION OF ANILINE ON δ -MANGANESE DIOXIDE POWDER AND PROPERTIES OF COMPOSITES, Ke-Cheng Gong, Wen Zhang, South China Univ of Technology, Polymer Structure & Modification Res Lab, Guang-Dong, CHINA.

Composite powders of polyaniline and δ -manganese dioxide has been successfully achieved by surface-induced polymerization of aniline on δ -manganese powder in an acid medium. The content of manganese dioxide in composites increased with increasing amount of manganese dioxide in polymerization bath. Conductivity of composites is affected by the molar ratio of manganese dioxide/aniline, acid concentration, and specific surface area of manganese dioxide powder. The maximum conductivity of composites can reach 1.1 S/cm. Aniline is oxidized in the surface of δ -manganese dioxide powder. When the molar ratio of δ -manganese dioxide/aniline is low, the crystal structure of manganese dioxide in composites is amorphous. δ manganese dioxide/polyaniline composites can be gotten in high molar ratio and their conductivity is 10^{-4} - 10^{-5} S/cm. The cyclic voltammetric switching curve of these composites in 1 M $LiClO_4$ /propylene carbonate electrolyte has showed one pair oxidation reduction peak. These composites can be used in lithium second battery as cathode active materials [1]

[1] Ali H. Gemeay, Hiroshi Nishiyama, Susumn Kuwabate and Hiroshi Yoneyama, J. Electrochem. Soc., 1995, 142 (12), 4190-4195.

V5.28
IN SITU NMR STUDY OF THE HYDROTHERMAL SYNTHESIS OF TEMPLATE-MEDIATED MICROPOROUS ALUMINOPHOSPHATE MATERIALS, Corinne M. Gerardin, Princeton Univ, Dept of Geosciences, Princeton, NJ; Mohamed Haouas, Univ Louis Pasteur, RMN et Chimie du Solide, Strasbourg, FRANCE; Francis B. L. Taulelle, Univ Louis Pasteur, Dept of Solid State Chemistry; Thierry Lousseau, Gerard Ferey, Univ de Versailles, Versailles, FRANCE; Jean Renaudin, Univ du Maine, Lab des Fluorures, Le Mans, FRANCE; Claude Estournes, IPCMS, Groupe des Matériaux Inorganiques, Strasbourg, FRANCE.

To elucidate the formation mechanisms of crystalline microporous materials prepared with structure directing agents under hydrothermal conditions, one need observe the hydrothermal medium while the microporous material forms. The objective is to observe the assembly of the molecular precursors in solution which can be identified and quantified using in situ NMR during the hydrothermal treatment. For this purpose we developed NMR tools and methods to perform in situ experiments up to 473K under autogenous pressures. First, we designed different tube valve NMR assemblies suitable for different solutions (glass, vespel, alumina tubes with titania valves and optional teflon inserts). The devices allow us to perform quantitative NMR experiments by simultaneously recording the signal of a reference during the synthesis. The method was applied to the formation of the $AlPO_4$ -CJ2 microporous phase prepared at 453 K from $Al(OPr)_3$, H_3PO_4 , NH_4F , diazabicyclooctane and H_2O . Kinetics of crystallization of the $AlPO_4$ -CJ2 material could be determined running in situ NMR experiments of all nuclei ^{31}P , ^{27}Al , ^{19}F , and ^{15}N . The observation and quantification of the different signals from the liquid phase together with the solid state NMR analysis of the solid products obtained at different steps of the synthesis allowed us to characterize first the kinetics of dissolution of

the precipitate which initially forms in the mixture, and secondly the formation of the intermediate aluminophosphate solid phase which appears together with $\text{AlPO}_4\text{-CJ2}$. This intermediate phase is unstable and dissolves after a while to form $\text{AlPO}_4\text{-CJ2}$. The systematic powder x-ray diffraction characterizations of the intermediate solids confirm the NMR observations. We also developed a method to determine the pH of an hydrothermal solution by NMR and we were able to follow the pH evolution by ^{14}N NMR of an amine during the $\text{AlPO}_4\text{-CJ2}$ synthesis. Using the different NMR tools to quantitatively characterize the hydrothermal medium while the synthesis proceeds can yield to a better description of the different steps of the materials formation.

SESSION V6: STRUCTURE-DIRECTED CONDENSATION PROCESSES

Chair: Brad D. Chmelka
Wednesday Morning, April 2, 1997
Nob Hill C

8:30 AM *V6.1

INTERFACIAL CONTROL MECHANISMS IN BIOMINERALIZATION, Daniel E. Morse, Univ of California-S Barbara, Dept of Biological Sciences, Santa Barbara, CA; Angela Belcher, Univ of California-S Barbara, Dept of Chem, Santa Barbara, CA; Charlotte M. Zaremba, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA; Deron Walters, Bettye Smith, Paul K. Hansma, Univ of California-S Barbara, Dept of Physics, Santa Barbara, CA; Galen D. Stucky, Univ of California-S Barbara, Dept of Chemistry, Santa Barbara, CA.

Nature uses two different mechanisms for directing structure during synthesis of the microlaminate composites of the abalone shell and flat pearl. One controls structure and orientation of the minerals at the atomic and nanoscale levels; the other controls ordering over macroscopic dimensions. Proteins of 3 families exert this control. A nucleating protein sheet, in conjunction with calcite-specific polyanionic proteins, directs nucleation of oriented calcite to form a primer. A genetic switch then controls the abrupt transition to synthesis of polyanionic proteins that direct deposition of aragonite on this primer. These polyanionic proteins control polymorph selection and determine orientation of the atomic lattice by cooperative interactions with inorganic ions at the growing crystal interfaces. Microlaminate nacre is organized over macroscopic dimensions by continuous crystallization of the atomically coherent protein-oriented aragonite through pores in a multilayered network of sheets of matrix proteins. Stochastic spacing of stencil-like nanopores in these interlamellar protein sheets determines the lateral offset between successive microlaminae, thus generating the interdigitating brickwork that gives the material its remarkable strength. Use of the purified polyanionic proteins allows us, in vitro, to abruptly and sequentially switch crystallographic phase from calcite to aragonite and vice-versa, in stereospecific directions, producing multiphase composites with micron-scale domains.

9:00 AM *V6.2

POLYMER INDUCED LIQUID-PRECURSOR PHASE IN CALCIUM CARBONATES: A NEW STRATEGY FOR BIOMIMETICS?, Laurie A. Gower, Univ of Massachusetts, Polymer Science & Engineering, Amherst, MA.

Unusual CaCO_3 structures, films, and coatings have been produced by the addition of low levels of polyaspartate to the crystallization medium. The mechanism which creates these thin (submicron) calcitic films has been elucidated by *in situ* optical microscopy. Phase separation of a hydrated CaCO_3 /polypeptide precursor creates isotropic droplets which spread and coat the substrate, and subsequently transform (dehydrate) into the birefringent films. This unusual liquid precursor is believed to arise from a dual action of the polyelectrolyte, i.e. through the concentration of ionic species, but with an inhibitory delay of the nucleation event. Fluorescent labelling techniques are being used to determine the role of the polymer in this precursor mechanism. Some of the features of this mechanism hint that a polymer induced liquid-precursor phase may play a role in biomineralization processes, and thus may provide new biomimetic strategies towards the fabrication of inorganic thin films, coatings, and meso-structures.

9:30 AM *V6.3

IN SITU MINERALIZATION OF HYDROGELS VIA EXTRUSION FREEFORM FABRICATION, Paul Calvert, Univ of Arizona, Dept of MS&E, Tucson, AZ; Zhengshe Liu, Univ of Arizona, Tucson, AZ.

Extrusion freeform fabrication is a 3-D layerwise writing technique for forming objects directly under the control of a CAD program. A fine needle extrudes an aqueous solution of gelling material, which is

written layer by-layer into objects. Mineralized gels are formed by extruding layers, each about 0.5 mm thick, containing high concentrations of calcium salts or of carbonate. By making an alternating stack of layers, mineralization occurs by diffusion of calcium and carbonate or phosphate between layers. As formed, such materials behave as stiff gels. When allowed to dry, they become hard bone-like composites. This process is viewed as a close analogy to the growth of bone where polymer layers are deposited and then mineralized. The influence of the gel matrix on the precipitate morphology and composite properties will be discussed.

10:00 AM V6.4

SYNTHESIS OF NANOSTRUCTURED TiO_2 BASED MATERIALS THROUGH CLUSTERS SELF-ASSEMBLING PROCESS, Abdelkrim Chemseddine, Thomas Moritz, Hahn-Meitner-Inst, Dept of Physical Chemistry, Berlin, GERMANY.

A new synthetic approach to create TiO_2 nanocrystallites with different shapes and sizes will be presented. The method is based on controlling the early stages of nucleation and growth using a cooperative formation of inorganic-organic interfaces. Orientational ordering of faceted nanocrystals in superlattices is achieved over micrometer length scales using short organic ligands. TEM micrographs and X-rays data will be presented. The formation of these ordered arrays will be discussed and compared with formation pathways of the well known mesoporous silicates.

10:45 AM *V6.5

IONIC INTERACTIONS AT THE HYDROXYAPATITE/COLLAGEN INTERFACE, Brent R. Constantz, Mark T. Fulmer, Ira C. Ison, Ben Lin, Norian Corp., Cupertino, CA.

The topic of mineralization of collagen has received significant attention. Several groups investigated the mechanism of nucleation of calcium phosphate mineral during mineralization of collagen. *In vitro* experiments have demonstrated that the process of mineral nucleation may be initiated and controlled by other organic molecules (like phosphoproteins, phospholipids or small acidic peptides rich in aspartic and glutamic acids).

We examined the process of mineralization without any mineral nucleating factors except collagen alone. We have observed direct nucleation of apatitic calcium phosphates in collagen in the absence of other non-collagenous organic molecules. Mineralization occurred in a purified collagen solution under high pH ($\text{pH} = 12$) conditions, with a continuous influx of Na_3PO_4 and CaCl_2 solution. Type I collagen from bovine Achilles tendon, purified from all glycosaminoglycans and non-collagenous proteins, was used for this study. Purity of collagen was tested by amino acid composition using HPLC. Transmission electron microscopy indicates that mineralization has occurred all the way around and inside the collagen fibrillar bundles. The mineral formed was analyzed using X-ray diffraction (XRD) and infrared spectroscopy (FTIR). Results showed that the mineral formed was carbonated and poorly crystalline hydroxyapatite which appears to be similar to bone mineral. We hypothesize that the net charges on the surface of the collagen are modified under elevated pH environment to attract the counter inorganic ions resulting in mineral nucleation of collagen. Such an environment may also exist during the initial *in vivo* stages of cell mediated osteoid collagen mineralization.

11:15 AM *V6.6

THE EFFECT OF SOME C_3 -SATURATED ORGANIC MOLECULES ON THE IN-VITRO PRECIPITATION OF HYDROXYLAPATITE, D. M. Corrand, J T Czernuszka, Univ of Oxford, Dept of Materials, Oxford, UNITED KINGDOM.

Bone and tooth specific proteins, as well as many inorganic chemicals, have been studied intensively and are now believed to influence both the *in situ* and/or the *in vitro* biomineralization process. However, their role in specific nucleation or as growth regulators during the formation of the hydroxyapatite crystals has not yet been completely understood. For these reasons, a project was initiated with the aim of assessing a series of biochemicals which possess either one or more of the active groups found along bone specific protein chains. They have been chosen to have a common number of carbon atoms, three in this case, which should make the interactions easier to assess than in the case of large multi-folded protein molecules. This study consists in using constant-composition coprecipitation experiments, with calcium and phosphate concentrations close to the human physiological case, coupled with SEM, TEM, FTIR, XRD and WDX analyses. The results showed that, in the case of a calcium/additive concentration ratio of one, the phosphorylated acids, such as Phosphoserine and Propylphosphonic Acid had the greatest influence on the final hydroxyapatite crystal morphology. In terms of crystal size reduction, the series can be ranked as follows: No Additives \approx Serine \approx AminoPropanol \leq Alanine $<$ Malonic Acid $<$ Phosphoserine $<$

Propylphosphonic Acid. The amphiphilic nature of Propylphosphonic appeared to be an additional parameter in the molecular crystal growth inhibitory activity. In order to follow precisely the influence of such biochemicals, a two-step experimental technique was used for the first time and seems more appropriate to the study of highly sensitive crystallization processes met under these experimental conditions. These effects can be explained in terms of nucleation rate and growth rate changes induced by organic/inorganic molecular interactions.

11:45 AM V6.7

SYNTHESIS OF POLYMERIC PSEUDOCROWN ETHER MEMBRANES USING POLY(ETHYLENE GLYCOL) DIACRYLATES AND TEMPLATING IONS, Brian John Elliott, Christopher N. Bowman, Univ of Colorado, Dept of Chemical Engr, Boulder, CO; Alec B. Scranton, Michigan State Univ, Dept of Chemical Engr, East Lansing, MI.

A novel method for producing inexpensive pseudocrown ether membranes in situ during free radical photopolymerization has been developed. This scheme is based on the concept of a templating ion which induces poly(ethylene glycol) diacrylates to form intramolecular cycles during photopolymerization. Poly(ethylene glycol) diacrylate monomers are complexed with metal ions prior to polymerization. Given that the diameter of the templating ion is an appropriate size, the monomer will wrap around the ion bringing the two reactive end groups into close proximity. This templating will result in increased primary cyclization (i.e. pseudocrown ether formation). Membranes are formed by photopolymerizing the templated diacrylate monomers either with or without comonomers and a non-polar solvent in the pores of a polyethylene membrane support. The templating ions are then removed by ion exchange with protons and the pseudocrown ether sites become locations for later metal adsorption. Pseudocrown ether membranes reject metal ions such as chromium, manganese, and zirconium from water. Rejection behavior is related to the reaction conditions of the membrane synthesis, the ionic charge of the metal and competitive effects from other ions in the feed. Rejection fractions as high as 0.8 for chromium, and 0.9 for zirconium have been obtained. Applications for these membranes include the removal of metals from hydrocarbon sources as well as from contaminated water sources. There are methods known today for removal of many of these contaminants; however, the search for more efficient and more economical solutions continues. Crown ethers themselves are expensive and toxic, and pseudocrown ether membranes offer an inexpensive, less toxic alternative.

SESSION V7: INORGANIC-ORGANIC INTERACTIONS IN SOL-GEL, SILICON CARBIDE, AND POLYMERIC SYSTEMS

Chair: Paul E. Laibinis

Wednesday Afternoon, April 2, 1997
Nob Hill C

1:30 PM *V7.1

INTERFACIAL EFFECTS AND CONTROLLED INTERFACES WITHIN SOL-GEL DERIVED HYBRID ORGANIC-INORGANIC SYSTEMS, Clement Sanchez, Univ Pierre et Marie Curie, Chimie de la Matière Condensée, Paris, FRANCE.

The various characteristics of sol-gel process (metallo-organic precursors, organic solvents, low processing temperatures) allow to introduce fragile organic molecules inside an inorganic network. The properties of hybrid materials do not depend only on organic and inorganic components but also on the interface between both phases. The general tendency is therefore to increase interfacial interactions by creating an intimate mixing, or interpenetration, between organic and inorganic networks. The formation of covalent chemical bonds or the tuning of weaker interactions (hydrogen bonds, van der Waals, electrostatic interactions) between organic and inorganic species allow to tailor hybrid materials properties. This conference will describe two of these aspects:

The tuning of optical properties (photochromic, emission...) by modification of the hybrid interface.

The building of sol-gel derived hybrid nanocomposites with better defined interfaces. These aspects will be illustrated with several examples of hybrid materials belonging to siloxane-oxide and to tin-oxo-related systems.

2:00 PM V7.2

CHARACTERIZATION OF POLYMER-DERIVED FINE SILICON CARBIDE FIBER, Wei Chen, Chris S. McMillan, Rebecca L. Durall, Dow Corning Corp, Dept of Analytical Sciences, Midland, MI; James A. Rabe, K. T. Nguyen, Dow Corning Corp, Ceramic Program, Midland, MI.

Small diameter silicon carbide (SiC) fibers, produced from a polymer

precursor route, have been used in composite materials. Boron compounds are introduced into SiC fibers during the manufacturing process to enhance fiber performances. The interfacial properties between fibers and composite matrices are believed to correlate to fiber surface properties. Additionally, since the SiC fibers typically have small diameters (10-15 μm), surface composition and species would likely impact fiber mechanical properties as well. Several surface analytical tools, scanning Auger microprobe (AES), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), have been employed to characterize various fibers fabricated under different processing conditions. The fibers obtained using our process typically show smooth surfaces and a dense interior. Although no obvious phase separation could be observed, a boron and carbon rich surface was detected for each fiber. The boron concentration decreases quickly in bulk while the silicon concentration increases gradually. The C/Si ratio reaches stoichiometry at a certain depth from the surface. Boron nitride was identified as one of the boron compounds on fiber surfaces. Other boron compounds are also present on the fiber surfaces depending on the processing conditions.

2:15 PM V7.3

MORPHOLOGY/BARRIER PROPERTY CORRELATION OF PLASMA-COATED SiO_2 FILMS ON POLYMER SUBSTRATES, Bo-Chy Wang, Richard J. Spontak, North Carolina State Univ, Dept of MS&E, Raleigh, NC; Yelena G. Tropsha, Erwin A. Vogler, Manoj Dalvie, Kevin D. Mar, Becton Dickinson Research Ctr, Dept of Polymer Sci & Tech, Research Triangle Pk, NC.

Transparent coatings capable of enhancing gas impermeability through polymers have recently received considerable attention in packaging and medical applications. Plasma-based processing affords the advantage of depositing multidirectional coatings and is particularly advantageous when complex 3-D shapes must be coated. In this work, analytical methods, such as energy-filtered transmission electron microscopy (EFTEM) and atomic force microscopy (AFM) have been successfully employed to help elucidate key relationships between the morphology of thin SiO_2 films and the barrier properties of coated polymers. It has been found that discrete particles constitute the principal morphological characteristics of plasma-deposited SiO_2 coatings on polystyrene and polycarbonate. The measured roughness of the thin coating is independent of the polymer substrate. Under controlled deposition conditions (e.g., power, pressure, flow rate and oxygen: hexamethyldisiloxane ratio), the particle characteristics remain consistent in both size and porosity. However, from AFM and ellipsometry, the porosity is power-dependent. A critical high power level is identified for producing films with consistently high barrier quality. Depositions conducted at low power, on the other hand, result in SiO_2 films of higher porosity and poorer barrier properties. Along with the data presented, a conceptual model will be introduced to interpret the observed relationships.

2:30 PM V7.4

STABILITY OF ANTHRACENE AND STILBENE ON NANOPOROUS SOL-GEL SURFACES, Guangming Li, Larry W. Burggraf, Air Force Inst of Technology, Dept of Engr Physics, Wright Patterson AFB, OH.

Anthracene and stilbene are well known as most important organic scintillators due to their very high efficiency and fast response. In this paper, we report our recent work in synthesis of anthracene and stilbene incorporated silica by sol-gel process. Enhanced chemical reactions such as isomerization and polymerization were observed on some strong acid surfaces like aluminosilicates. The chemical stability of anthracene and stilbene in different nanoporous sol-gel oxides (silica and aluminosilicate) were investigated by means of optical absorption, fluorescence, FTIR and Raman spectroscopies. It is found that the anthracene and stilbene molecules in the nanoporous sol-gel materials exhibit rather different properties from what are expected under normal conditions (in air, solvent or nonporous surface).

3:15 PM V7.5

INVESTIGATION OF NEW-ION CONDUCTING ORMOLYTES SILICA-POLYPROPYLENEGLYCOL, Mauricio Simoes de Lima, Univ de Sao Paulo, Inst de Fisica de Sao Carlos, Sao Carlos, BRAZIL; Karim Dahmouche, Univ Estadual Paulista, Dept de Fisico-Quimica, Araraquara-SP, BRAZIL; Clovis Ribeiro, Univ Estadual Paulista, Dept de Quimica Analitica, Araraquara, BRAZIL; Sandra H. Pulcinelli, Celso V. Santilli, Univ Estadual Paulista, Dept de Fisico-Quimica, Araraquara, BRAZIL.

Two families of Hybrid Organic-inorganic composites exhibiting ionic conduction properties, so-called ORMOLYTES (organically modified electrolytes), have been prepared by the sol-gel process. The family I has been prepared from mixture of 3-isocyanatopropyltriethoxysilane (IsoTrEOS), O,O'-Bis(2aminopropyl) polypropyleneglycol and lithium salt. These materials present chemical bonds between the organic (polymer) and inorganic (silica) phases. The family II has been

prepared by ultrasonic method from a mixture of tetraethoxysilane (TEOS), polypropyleneglycol and lithium salt. The organic and inorganic phases are not chemically bonded in these samples. The Li^+ ionic conductivity σ of all these materials has been studied by AC impedance spectroscopy up to 100°C . Values of σ up to $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ have been found at room temperature. A systemic study has been done changing the lithium concentration, the polymer chain length, and the polymer to silica ratio, and shows the strong dependance of σ with the preparation conditions. Thermal mechanical analysis measurements between -100°C and 100°C have shown a polymeric behavior for both families of materials. A correlation between the vitreous transition temperature of the samples and their ionic conductivity has been observed. At least, a better knowledge of the gelification mechanisms in these system has been obtained, studying the evolution of their rheological properties as a function of time. The structures, the mechanical and the ionic conduction properties of both families were compared with emphasis on the nature of the bonds between the organic and inorganic components.

3:30 PM V7.6

STUDIES OF THE THIN-FILM STRUCTURE OF POLYSILAETHYLENE: AN ORGANIC/INORGANIC HYBRID POLYMER WITH AN ALTERNATING C/Si BACKBONE,
Mei-Wei Tsao, John F. Rabolt, Univ of Delaware, Dept of Materials Science, Newark, DE; Karl-Heinz Pfeifer, Univ of Heidelberg, Dept of Chemistry, Heidelberg, GERMANY; D. B. Holt, Barry L. Farmer, Univ of Virginia, Dept of MS&E, Charlottesville, VA; Qionghua Shen, Len Interrante, Rensselaer Polytechnic Inst, Dept of Chemistry, Troy, NY.

Advanced polymeric thin film materials of the future will contain not only organic or inorganic substituents, but will also be hybrid systems containing both in such proportions so as to optimize both properties and processability. To this end, polysilaethylene ($[\text{SiH}_2\text{CH}_2]_n$) (PSE) and deuterated polysilaethylene ($[\text{SiD}_2\text{CH}_2]_n$) have been examined by both vibrational spectroscopy and x-ray diffraction methods above and below the crystallization/melting transition at -20°C . The results confirm previous speculations that PSE crystallizes in an all trans conformation analogous to that found for its all-carbon analog, polyethylene. PSE thin films were studied, both above and below the melting transition, by the use of vibrational spectroscopy and tapping mode AFM with phase detection ability. The conformation/morphology of these two phases show a dramatic difference. PSE is a potential silicon carbide precursor in polymer form. Thin SiC coatings can be easily deposited through the use of standard polymer processing techniques.

3:45 PM V7.7

STRUCTURE-DETERMINING FACTORS IN METHACRYLATE-SUBSTITUTED METAL OXO-CLUSTERS,
Ulrich Schubert, Guido Kickelbick, Technische Univ Wien, Inst of Inorg Chemistry, Vienna, AUSTRIA.

Reaction of methacrylic acid (McO-H) with metal alkoxides, E(OR)_n , leads to new molecular precursors $\text{E(OR)}_{n-x}(\text{OMc})_x$. They are often used for the preparation of inorganic-organic hybrid polymers by sol-gel processing, followed by polymerization of the organic groups. The structural organization of the building blocks from which the polymers are composed determines the properties of such materials. An understanding of the basic structures therefore is the key for a deliberate materials design.

The isolation and structural characterization of the two methacrylate substituted zirconium oxo-clusters $\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OMc})_{12}$ and $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ and their comparison with the previously determined structure of $\text{Ti}_6\text{O}_4(\text{OEt})_8(\text{OMc})_8$ allows the elaboration of the factors that influence the structural organization of such inorganic organic solids. The aptitude of zirconium to adopt higher coordination numbers than titanium has immediate consequences on the maximum number of polymerizable Omc ligands per metal atom and on the linkage of the coordination polyhedra of the metal atoms.

4:00 PM V7.8

STRUCTURAL CHARACTERIZATION OF HYBRID POLY-DIMETHYLSILOXANE-OXIDE SYSTEMS,
Florence Babonneau, Univ Pierre et Marie Curie, Dept of Chemistry of Condensed Materials, Paris, FRANCE; Sandra Dire, Univ di Trento, Dept di Ingegneria dei Materiali, Trento, ITALY.

Sol-gel processing of hybrid siloxane-oxide materials is an area of rapid growth due to the wide variety of potential applications of these systems. The flexibility offered by this synthetic approach large variety of precursors; low temperature could allow real molecular engineering of the final materials that could eventually lead to controlled nanostructures.

Various polydimethylsiloxane-oxide related systems were prepared starting either from monomeric species such as dimethyl

diethoxysilane, or OH-terminated short polydimethylsiloxanes. The oxide component was introduced via metallic alkoxides, M(OR)_n ($\text{M} = \text{Si, Ti, Zr}$). Transparent materials from flexible to brittle gels can be obtained over a large M/siloxane range.

The structure of the various systems have been investigated by spectroscopic techniques: MAS-NMR (^{29}Si , ^{13}C and ^1H), x ray absorption (Ti and Zr K edge), Infrared and Raman. Depending on the nature of M and of the M/siloxane ratio, structural models are proposed, ranging from single phase systems with high interconnection between siloxane and oxide units, to nanocomposites with chains of polysiloxanes crosslinked with oxide-based particles.

4:15 PM V7.9

THE INVESTIGATION OF POLYMER-INORGANIC INTERFACE BY VERY COLD NEUTRON TOTAL REFLECTION PHENOMENON, Sergey S.P. Kuznetsov, Anatoliy A.D.

Perekrestenko, Aleksey A. I. Isakov, Lebedev Physics Inst, Moscow, RUSSIA; Anatoliy A. V. Shelagin, Moscow Physical & Tech Inst, Dolgoprudnyi, RUSSIA; Igor I. V. Meshkov, Lebedev Physics Inst, Moscow, RUSSIA; Dmitriy D. A. Shelagin, Moscow Physical & Tech Inst, Dolgoprudnyi, RUSSIA; Vadim V. G. Krashennnikov, Lyudmila L. A. Novokshonova, Natalya N. Yu. Kovaleva, Semenov Inst of Chemical Physics, Moscow, RUSSIA.

The investigation of thin layers (thickness 30 nm) supermolecular structure (SMS) of polymer near the polymer-inorganic interface have been carried out by very cold neutrons (VCN) spectrometer. All specimens were obtained by deuterium polyethylene and polyethylene polymerization directly on the silicon surface activated by catalyst. The wavelength dependences of reflection coefficient (R) have been measured in the range from 4 to 40 nm at the constant reflection angle -60 degrees. The total VCN reflection phenomenon were observed on polyethylene-silicon and silicon-deuterium polyethylene interfaces and the diffusion in the main VCN reflection from deuterium polyethylene external surface were observed too. Thus, the analysis of form and amplitude of wavelength R dependences showed that SMS of polymer near the polymer-inorganic interface is more ordered than the same near the external surface of polymer obtained by direct polymerization technology. The density of polymer near the polyethylene-silicon interface were obtained (1.1 g/cubic cm) by fixing the point (wavelength) of VCN total reflection phenomenon.